Studies on A. C. Polarography. IV. Reversible Behaviour of Anions

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Introduction

A comprehensive polarographic investigation of various anions was carried out by Revenda,[1] and Kolthoff and Miller,[2] who introduced the polarographic equations of those anions depolarizing the dropping mercury anode. Recently, Breyer et al.[3] have communicated many investigations on a. c. polarography of anions, using an a. c. polarographic equipment, and have shown that the summit-potential of an a. c. polarogram does not agree with the half-wave potential of the ordinary polarogram and also that the shape of Breyer's polarogram is unsymmetrical, which is different from the fact found in the case of cations.

In the previous paper, the theoretical equation representing the a. c. electrolytic current in a. c. polarography was introduced by Tachi and others[4] and it has been confirmed that Breyer's polarogram is a derivative curve of the ordinary polarogram, provided that the depolarizing process is reversible. And now, the authors will show the results of the experiments in which they attempted to discover whether Breyer's polarogram of anions would agree with the derivative curve led from the equation of the polarographic diagram introduced by Kolthoff and Miller. And also, the experimental results of the behaviour of d. c. component in a. c. polarography, i. e. Fournier's current, and the relationship between the concentration of the depolarizer and the polarographic current intensity of Breyer's polarograms will be reported.

Experimental

The anions used here as the depolarizer were Cl^-, Br^-, I^-, $S_2O_3^=$ and CN^-, which are in the form of KCl, KBr, KI, $Na_2S_2O_3$ and KCN respectively. They were polarographed in the concentration range from 10^{-4} N to 10^{-2} N for the ease of comparing Breyer's polarogram with the ordinary polarogram, since the ordinary polarograms of anions, especially halogen ions, in the concentration higher than 10^{-3} N are not well-defined in general.

The concentration of KNO_3 aq. solution as the supporting electrolyte was made 0.2 N to keep the low impedance of the solution in the polarographic cell. But in the case of polarographic electrolysis of CN^-, 0.2 N NaOH aq. solution was used instead of 0.2 N KNO_3 aq. solution.

The circuit of a. c. polarography used was the same one as described in the previous papers. A pool condenser (50μF electrolytic condenser) was always connected between the bottom mercury and reference electrode in order to decrease the impedance of the liquid junction. In the case of polarographing Breyer's polarogram, the amplitude of a. c. voltage superimposed upon d. c. voltage was kept always 50 mv (60 c/s), and in registering Fournier's polarogram, it was changed from 0 to 100 or 120 mv (60 c/s).

The drop time of mercury electrode was 4.6 sec. and the rate of mercury flow was 2.2 mg/sec. (at O v *vs.* N.C.E.). The normal calomel electrode was employed as the reference electrode. All measurements were carried out at room temperature (about 17°C). The sensibility of the galvanometer was 2.87×10^{-9} amp./mm/m.

Experimental Results and Discussion

(1) The Shape of Breyer's Polarogram

(i) ***Cl^-, Br^-, I^-.***—Kolthoff and Miller gave the following equation for the polarographic wave of the depolarizers which form slightly soluble mercurous compounds at the dropping mercury electrode

$$i=\begin{cases} i_d-\exp\dfrac{-F(E-E_o')}{RT} & \text{for } E\geqq E_{st} \\ O & \text{for } E\leqq E_{st} \end{cases} \quad (1)$$

where E_{st} represents the starting potential of the ordinary polarogram, and E_o' is determined by the solubility product of the mercurous compound formed at the anode, and i_d is the limiting current of the polarographic wave and the positive sign of i means the anodic current. Thus the derivative curve of the ordinary polarogram is given by

$$\frac{di}{dE}=\begin{cases} \dfrac{F}{RT}\exp\dfrac{-F(E-E_o')}{RT} & \text{for } E\geqq E_{st}, \\ O & \text{for } E\leqq E_{st}. \end{cases} \quad (1a)$$

1) J. Revenda, *Collection Czech. Chem. Communs.*, 6, 453 (1934).
2) I. M. Kolthoff and C. S. Miller, *J. Am. Chem. Soc.*, 63, 1405 (1941).
3) B. Breyer, F. Gutman and S. Hacobian, *Aust. J. Sci. Res.* **A3**, 558, 567, 595 (1950), **A4**, 611 (1951).
4) I. Tachi, et al., This Bulletin 28, 25, 31, 37, (1955).

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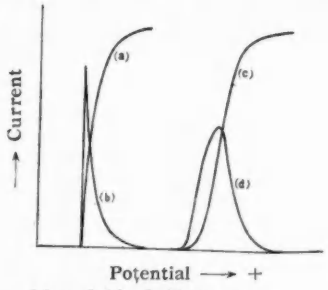
The curves represented by the equations (1) and (1a) are illustrated in Fig. 1 (a) and (b).



(a) and (c); i—E curve
(b) and (d); di/dE—E curve.

Fig. 1. The model curves of the ordinary polarographic wave and the derivative polarographic wave.
(a) i—E curve in the case of Cl^-, Br^- and I^-.
(b) di/dE—E curve of the upper.
(c) i—E curve in the case of $S_2O_3^=$ and CN^-.
(d) di/dE—E curve of the upper.

Now, assuming that Breyer's polarogram would be given by the derivative curve of the ordinary polarogram as stated in the introduction, Breyer's polarographic wave is supposed to be the curve whose peak potential agrees with the starting potential of the ordinary polarographic wave.

The experimental results are shown in Table I and Fig. 2 (a), (b) and (c), and it is recognized that the summit potentials of Breyer's polarograms (E_s) generally coincide with the starting potentials of the ordinary polarograms (E_{st}) except in the case of Br^-, whose E_s always agrees with the potential at which a kink appears on the ordinary polarogram. Further, this kink suggests that the ordinary polarogram of Br^- consists of two steps, of which the first step may be due to the adsorption of Br^- at the electrode. The reasons are as follows.

The fact that the shape of Breyer's polarogram of Br^- is different from those of Cl^- and I^- in the point of having a prewave adjoining the main wave (Fig. 3), shows that another increase of the admittance at the dropping mercury electrode occurs at more negative potentials than E_s of Breyer's

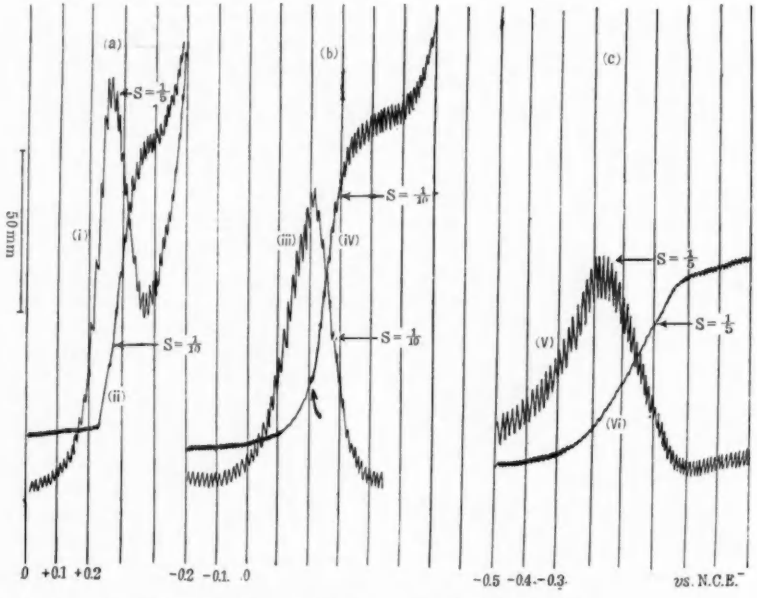


Fig. 2. Breyer's and the ordinary polarogram of Cl^-, Br^- and I^-.
(i) Breyer's polarogram of 6×10^{-4}N Cl^-.
(ii) Ordinary polarogram of (i).
(iii) Breyer's polarogram of 8×10^{-4}N Br^-.
(iv) Ordinary polarogram of (iii).
The arrow points the kink on the ordinary polarogram of Br^-.
(v) Breyer's polarogram of 1×10^{-3}N I^-.
(vi) Ordinary polarogram of (v).

TABLE I

Depolarizer	Potential *vs.* N. C. E.	Conc. $\times 10^4$ N 2	4	6	8	10
		(V)	(V)	(V)	(V)	(V)
	E_s	0.270	0.260	0.240	0.230	0.230
Cl^-	$E_{1/2}$	0.275	0.275	0.275	0.280	0.280
	E_{st}	0.250	0.240	0.230	0.220	0.210
	E_s	0.160	0.140	0.120	0.110	0.100
Br^-	$E_{1/2}$	0.150	0.140	0.160	0.150	0.150
	E_{st}	0.100	0.090	0.050	0.090	
	E_s	−0.170	−0.170	−0.160	−0.170	−0.180
I^-	$E_{1/2}$			−0.025	−0.030	−0.060
	E_{st}			−0.210	−0.210	−0.200
	E_s	−0.140	−0.165	−0.180	−0.200	−0.220
$S_2O_3^=$	$E_{1/2}$	−0.100	−0.110	−0.120	−0.120	−0.120
	$E_{(\sqrt{2}-1)id}$	−0.130	−0.135	−0.145	−0.150	−0.150
	E_s	−0.320	−0.330	−0.330	−0.335	−0.335
CN^-	$E_{1/2}$	−0.335	−0.340	−0.340	−0.340	−0.350
	$E_{(\sqrt{2}-1)id}$	−0.340	−0.350	−0.355	−0.355	−0.355

E_s: Peak potential of Breyer's polarogram.
$E_{1/2}$: Half-wave potential of the ordinary polarogram.
E_{st}: Starting potential of the ordinary polarogram.
$E_{(\sqrt{2}-1)id}$: Potential of the inflection point of the ordinary polarogram, namely the potential at which $i=(\sqrt{2}-1)i_d$.

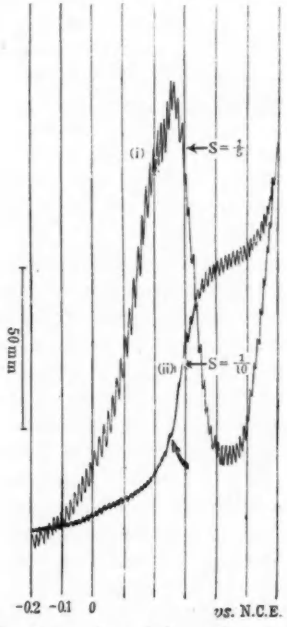


Fig. 3. Breyer's and the ordinary polarogram of Br^- with gelatine.
(i) Breyer's polarogram of 5×10^{-4}N Br^- with gelatine.
(ii) Ordinary polarogram of (i). The arrow points the kink on the ordinary polarogram of Br^-.

polarographic wave of Br^-, owing to the adsorption of the surface-active bromide ion. And the fact that the height of the prewave in the ordinary polarogram does not vary with the change of the concentration of the depolarizer suggests that the prewave may be due to the electro-oxidation of bromide ions oriented at the surface of the dropping mercury electrode.

(ii) *$S_2O_3^=$ and CN^-*.—Kolthoff and Miller introduced the following equation for the polarographic wave of depolarizers, which form slightly dissociated mercuric compounds or stable complex ions with mercuric ion; it can be written in the form

$$i=i_d+\frac{1}{2}\exp\frac{-2F(E-E_o')}{RT}-\frac{1}{2}\sqrt{4i_d\exp\frac{-2F(E-E_o')}{RT}+\exp\frac{-4F(E-E_o')}{RT}} \quad (2)$$

It follows therefore that

$$\frac{di}{dE}=-\frac{F}{RT}\left\{\frac{2i_d+\exp\frac{-2F(E-E_o')}{RT}}{\sqrt{4i_d\exp\frac{2F(E-E_o')}{RT}+1}}-\exp\frac{-2F(E-E_o')}{RT}\right\} \quad (2a)$$

From these equations, it will be shown that the potential (E_s), where di/dE becomes maximum, namely the inflection point of the equation (2), is to be the potential ($E_{(\sqrt{2}-1)id}$) given by $i=(\sqrt{2}-1)i_d$. Therefore, it is seen that the model curve of Breyer's polarogram of these anions is to be the curve which is unsymmetrical and have the peak potential (E_s) at the potential ($E_{(\sqrt{2}-1)id}$) of the ordinary polarogram as shown in Fig. 1 (d).

The experimental results obtained with $S_2O_3^=$, CN^- are shown in Tabe I and Fig. 4 (a) and (b). It was found that E_s was near to $E_{(\sqrt{2}-1)id}$, though the sharp agreements of these two potentials were not obtained, in the case of CN^-. But E_s of $S_2O_3^=$ shifts remarkably to more negative potential than $E_{(\sqrt{2}-1)id}$ of the ordinary polarogram, for which the reason is not clear and a further study is necessary.

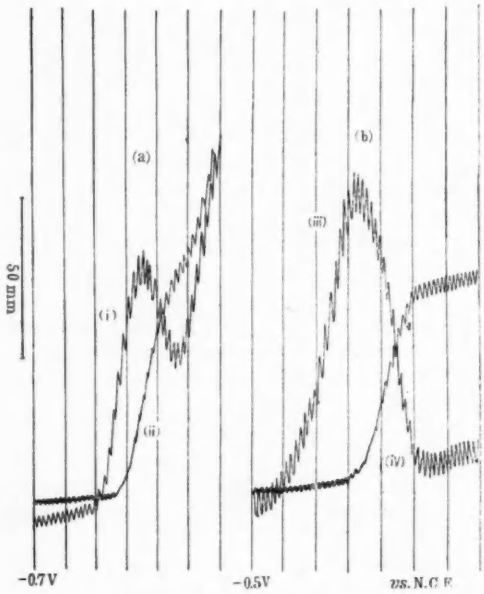


Fig. 4. Breyer's and the ordinary polarogram of $S_2O_3^=$ and CN^-.
(i) Breyer's polarogram of 6×10^{-4}N CN^-.
(ii) Ordinary polarogram of (i).
(iii) Breyer's polarogram of 6×10^{-4}N $S_2O_3^=$.
(iv) Ordinary polarogram of (iii).

(2) Fournier's Polarogram.—In this section, it will be reported that the experimental results as to the d. c. component in the a. c. polarography, i. e. Fournier's current, i_{Four}, generally agree with the theoretical consideration that Fournier's current observed by a galvanometer would be the mean value of the ordinary polarographic currents at both extreme potentials given by the superposition of small a. c. voltage (ΔE) on the d. c. potential, namely; $i_{Four}=\frac{1}{2}(i_{E-\Delta E}+i_{E+\Delta E})$.

Then the curves of Fournier's polarograms of Cl^-, Br^- and I^- are given by

$$i_{Four}=i_d-\exp\frac{-F(E-E_o')}{RT}\cdot\cosh\frac{E}{RT}\Delta E \qquad (3)$$

Thus from equations (1) and (3), it follows that

$$i-i_{Four}=\exp\frac{-F(E-E_o')}{RT}\cdot\left(\cosh\frac{F}{RT}\Delta E.-1\right)\geqq 0. \qquad (4)$$

Whence it follows that

$$i\geqq i_{Four}. \qquad (5)$$

Namely, Fournier's current increases more slowly than the ordinary polarographic current with increasing positive potential.

Next, in the case of $S_2O_3^=$ and CN^-, the equation representing Fournier's theoretical polarogram is comparatively complicated so that we merely assume that Fournier's polarogram would be less steep than the ordinary polarogram and the former would cross the latter at the inflection point of the ordinary polarogram.

The experimental results shown in Fig. 5 agree with the theoretical consideration. The fact that Fournier's polarogram of $S_2O_3^=$ crosses the ordinary polarogram at a more negative potential than that of the inflection point is not theoretically clear as well as the above mentioned discrepancy between E_s and $E_{(\sqrt{2}-1)id}$, and a further investigation will be necessary for the complete explanation of it.

(3) The Dependency of Breyer's Polarographic Current and the Ordinary Polarographic Current on the Concentration of Depolarizers.—The relationship between Breyer's polarographic current and the concentration of depolarizer is shown in Fig. 6. The relationship between the ordinary polarographic current and the concentration of the depolarizer is shown in Fig. 7.

5) M. Fournier, *Comp. Rend.*, 237, 1673 (1951).

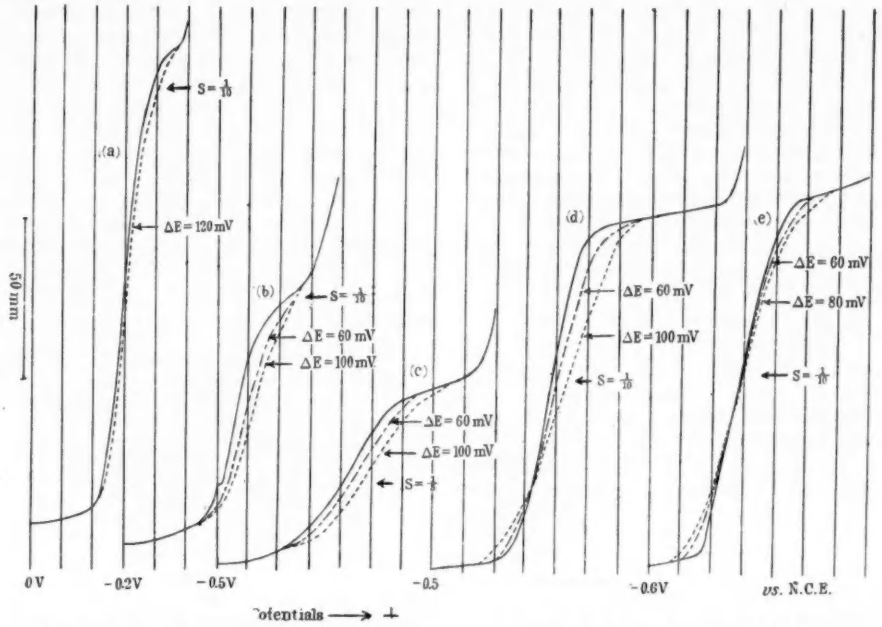


Fig. 5. Fournier's polarogram indicating the reversible electrode reactions of the named anions.
(a) 1×10^{-3}N Cl^-. (b) 6×10^{-4}N Br^-. (c) 1×10^{-3}N I^-. (d) 1×10^{-3}N $S_2O_3^=$.
(e) 1×10^{-3}N CN^-.
The ordinary poralogram is demonstrated by full lines, and Fournier's polarograms are indicated by dotted lines.

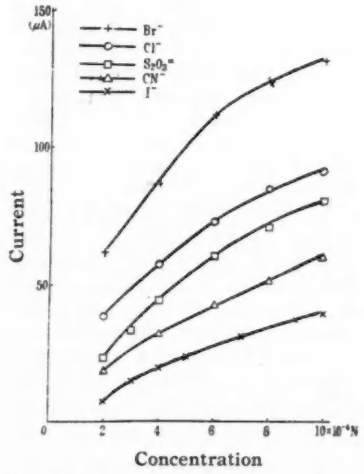


Fig. 6. The relationship between Breyer's polarographic current intensity and the concentration of depolarizer.

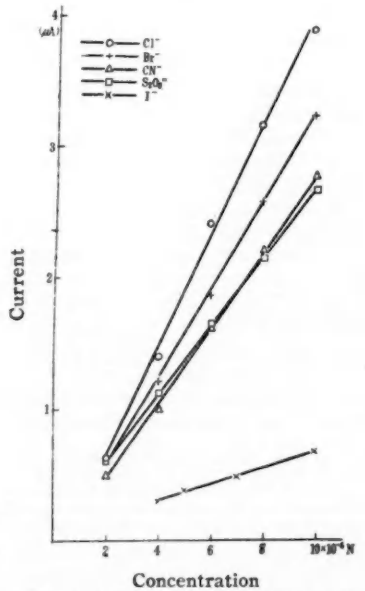


Fig. 7. The relationship between the ordinary polarographic current intensity and the concentration of the depolarizer.

The experimental results show that the linearity of the former holds generally over the concentration range from 2×10^{-4} N to 8×10^{-4} N, while the latter is linear over a tenfold concentration range. The non-linearity in a. c. polarography is probably due to the external impedance caused in the circuit. And the application of a. c. polarographic method to the quantitative determination of the anions is considered to be available, and for that purpose it must be cautioned that the external impedance in the circuit should be kept negligibly small.

Summary

A train of a. c. polarographic investigations on several anions, which depolarize the dropping mercury anode, was carried out. The experimental results of a. c. polarography of Cl^-, Br^-, I^- and CN^- generally agreed with the theoretical consideration based on the reversible electrode process. Namely, it can be concluded that Breyer's polarogram shows the derivative curve of the ordinary polarogram and Fournier's current of these anions is regarded as the mean of two current intensities at both the extreme potentials of the pulsing potential produced by the superposition of a small a. c. voltage on the ordinary d. c. potential. Thus the electrode processes of these anions are found to be reversible. And the possibility of the application to the quantitative determination of these anions was found in the proper concentration range.

The authors are indebted to the polarographic group to which we belong for their advice during the course of the research.

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Microscopic Studies on Fused Catalysts for Ammonia Synthesis. IV. Decomposition of Ammonia over Two Different Constituents

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Introduction

Many works on the iron catalyst for ammonia synthesis have been reported by many authors for these forty years. Many interesting results have been obtained about the role of potash added to the catalyst. But, so far as I am aware, no one has ever noticed the microscopic heterogeneity of the fused oxide, both before and after reduction.[1)]

As reported in our previous papers[2)], the optical, the surface-electron and the surface-ion microscopy revealed that the polished surface of some mixed catalysts in the unreduced state consists of two different sorts of grains. Of twelve catalysts investigated only those with potash or potash-alumina addition belong to this class.

Grains of the one sort (B) are found mainly along the boundaries of grains of the other sort (A), and the total quantity of B is very much less than that of A. B grains were found incidentally to be much less ferromagnetic than A grains. This fact furnished us with a convenient magnetic method of separating B grains from A grains. Chemical analysis showed that B powder was richer in K_2O than A powder. X-ray examination[3)] showed that A powders separated from different sorts of catalysts always possessed the pattern of spinel lattice of magnetite, and B powders, on the other hand, highly complicated patterns which differed slightly from each other and probably belonged to slightly modified lattices of magnetite with reduced degrees of symmetry. It was suggested that magnetite would not contain more than about 0.5 per cent of potash in its lattice, so that during solidification B crystals would segregate to take over its

1) In one of our previous papers[3)] B grains have been considered to be formed only in fused oxides rich in alumina and potash. Later experiments, however, showed that potash exess alone was sufficient for their formation.

2) N. Sasaki and Y. Ōsumi, *J. Chem. Soc. Japan (Pure Chemistry Section, Japanese)*, **73**, 808 (1952); Y. Ōsumi, ibid., **74**, 308 (1953). More details of the results of optical-, electron- and ion-microscopy are found in: a) Y. Ōsumi, "*Ammonium sulfate Engineering*" (*in Japanese*) **16**, 13 (1952). b) Y. Ōsumi, ibid., **17**, 8 (1953). c) Y. Ōsumi, ibid., **18**, 11 (1953).

3) Y. Ōsumi, This Bulletin, **26**, 519, (1953). Y. Ōsumi, "*Ammonium Sulphate Engineering*" (*in Japanese*) **18**, 14 (1953).

exess[4]).

The present paper deals with the activities for the decomposition of ammonia at about one atmospheric pressure of A and B powders separated from an ordinary doubly promoted catalyst.

Apparatus, Procedure and Preliminary Test.—Since the separation of B powder is tedious work a very small quantity of it (0.5 g.) was taken for the experiment and accordingly a very low flow rate (3.8 cc. per minute) had to be chosen, so that an unusual type of gas analysis was employed (Fig. 1).

e. a ⟶ b ⟶ c,·····c ⟶ b ⟶ a.

Catalyst powders were placed in the lower halves of horizontal reaction tubes, which were of terex glass, 4.3 mm. in inner diameter and 60 mm. long (Fig. 1c). Each was inserted in one of three tunnels bored through a copper block which could be heated electrically (Fig. 1b). The size of capillary tube 17 is such that while the largest part of the gas coming from the reaction tubes is sucked into the absorber where high vacuum prevails at the beginning, a certain small fraction of it still flows through stop cocks 18 and 19 into the atmosphere. This can be ascertained by means of flowmeter 16 by closing stop cock 18

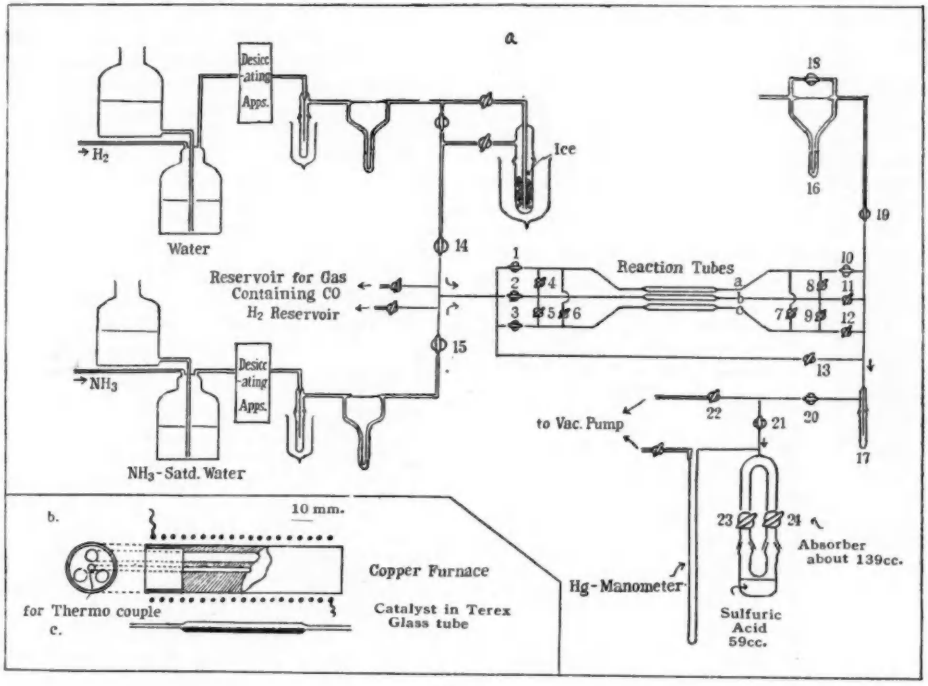

Fig. 1.

Electrolytic hydrogen gas was purified by passing through the solutions of potassium permanganate and potassium hydroxide, and over red hot copper, potassium hydroxide, and phosphorus pentoxide. Synthetic ammonia gas was dried over solid potassium hydroxide. The flow rate of each gas was kept nearly constant by inserting a buffer gas holder with large liquid levels before a capillary tube maintained at 25°C. In Fig. 1 straight lines beginning at stop cocks 14 and 15 show a system of capillary tubes, 1.5mm. in inner diameter. The gas can flow through three reaction tubes a, b and c in six different orders, i. for a short time. Thus the pressure inside the reaction tubes can always be kept slightly higher than one atmosphere.

The analysis of the gas from the reaction tubes is carried out in the following way: after evacuating the absorber (with stop cocks 21–24 open and 20 closed), the gas is sucked into the upper part of the absorber (with stop cocks 22–24 closed and 20–21 open) up to the pressure of about 400 mm Hg, and stop cock 21 is closed. Cock 23 is then opened as slowly as possible and then 24 is opened. The gas now begins to circulate in the absorber and ammonia is absorbed rapidly.

A certain amount of unreduced catalyst powder was divided into three parts. Each was placed in one of the reaction tubes connected in series and reduced at the same time. Our purpose was

4) From thermomagnetic measurements the possible existence of more than one magnetic phase in highly promoted catalysts has been concluded by L. R. Maxwell, J. S. Smart and S. Brunauer, *J. Chem. Phys.*, **19**, 303 (1951).

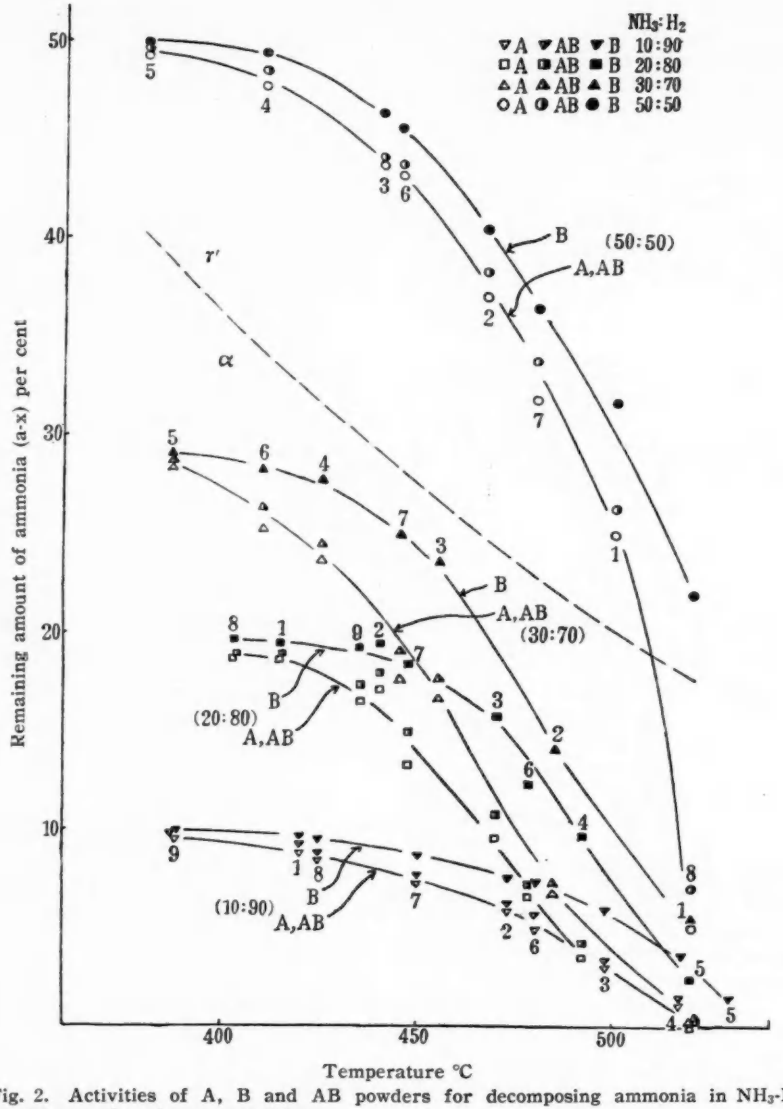

Fig. 2. Activities of A, B and AB powders for decomposing ammonia in NH_3-H_2 mixtures of various compositions.

(1, 2, 3,.....and a, b, c.....in the figure indicate the chronological order of data.)

From the ammonia per cent in original gas mixture (a) and that in decomposed gas mixture (b), the decomposed or remaining amount (x or a-x) was calculated as following:

$$H_2 + NH_3 \longrightarrow H_2 + NH_3 + N_2$$
$$100-a \quad a \quad 100a-+3/2x \quad a-x \quad 1/2x$$

therefore $b/100=(a-x)/(100+x)$, $x=100\ (a-b)$.

to see whether the catalysts so prepared were equally active toward ammonia decompositions. Hydrogen gas was passed through the tubes in the order a ⟶ b ⟶ c for seven hours each at 350°C, 400°C, 450°C, 500°C successively and then for fourteen hours at 530°C, the flow rate being 2.7 cc. per minute. After the reduction the activity of the catalyst at several temperatures between 400°C and 500°C was measured separately for each tube by passing a mixture of ammonia and hydrogen gas (3 : 7 in volume) at the rate of 3.7 cc. per minute through it. It was found that the activity decreased in the order a ⟶ b ⟶ c.

The reduction was then further continued by

passing hydrogen gas at 2.7 cc. per minute in the order c ⟶ b ⟶ a for seventeen hours and then in the order b ⟶ c ⟶ a for twenty-eight hours at 530°C. The three reaction tubes showed almost no difference in activity. The same was also the case when hydrogen gas at the rate of as high as 40 cc. per minute, was passed over the fresh oxide powder in one direction a ⟶ b ⟶ c only, the time and temperature schedule being the same as in the first instance. It may be inferred that the existence of a small amount of water vapour in hydrogen gas has a detrimental action.

Between runs the cold catalysts stood in hydrogen at about 800 mm Hg in order to prevent the intrusion of air.

Activity of A and B Powders toward Decomposition of Ammonia in Ammonia-Hydrogen Mixtures of Various Composition.—B powder amounting to about 3 per cent was separated from catalyst No. 4[5]. 0.5 g.[6] of each powder A, B and the original unseparated powder AB of the same mesh size (under about 300) was placed in three different tubes and reduced at the flow rate of 40 cc. per minute for 6 hours each at 300°C, 350°C, 400°C, 450°C, 470°C, 500°C and 520°C. In order to make the condition of reduction in each tube as equal as possible, the order of gas flow was altered every hour from one to another of the six ways. The ammonia-hydrogen gas mixtures for the decomposition test had the mixing ratios in volume, namely, 10: 90, 20: 80, 25: 75, 30: 70 and 50: 50. The results are shown in Fig. 2, the remaining amount of ammonia being expressed in % of the undecomposed original mixture. For all gas mixtures A and AB powders showed similar activity which was higher than that of B powder. The decomposed amount of the gas mixture 50: 50 is smaller than that of the mixture 30: 70 below about 500°C, but the situation is reversed above that temperature. This fact can be related to the work of Lehrer[7], who showed that four sorts of nitrides are formed by the action of mixtures of ammonia and hydrogen when the gas composition and temperature are suitably varied. It is significant that the broken line in Fig. 2 showing the boundary of α and γ' nitrides crosses the curve for the 50: 50 mixture at about 500°C. The apparent energy of activation roughly calculated from the curves for the mixture 30: 70, was found to be 30 kcal. for B powder and 25 kcal. for A powder.

The Poisoning Effect of Water Vapour and Carbon Monoxide.—The influence of water vapour upon the activity was tested with three sorts of powders A, B and AB of catalyst No. 4. Hydrogen was passed through a bottle filled with crushed ice and placed in a bath kept at −7°C and then mixed with ammonia to the composition NH_3: H_2=1:3 (Fig. 1a, Water vapour pressure over ice at

5) An iron catalyst including Al_2O_3 (5%), and K_2O (1%).

6) For the scientific purpose activity per unit area of catalyst would be more significant than activity per unit mass. The measurement of the surface area is planned.

7) E. Lehrer, *Z. Elektrochem.*, **36**, 383 (1930).

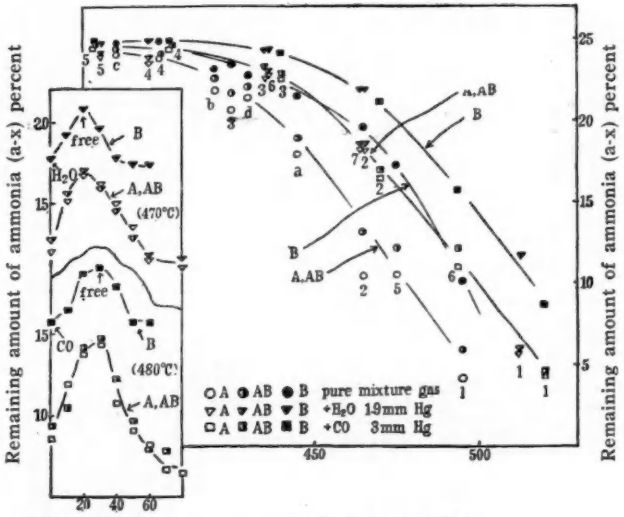

Fig. 3b.

Fig. 3a. Poisoning effects of water vapour and carbon monoxide.

−7°C is 2.54 mm Hg). The results are shown in Fig. 3a. A (AB) and B powders all show similar decreases in activity.

Carbon monoxide affected the activity to nearly the same extent, when the gas mixture was led to the reaction tubes from a gas holder in which 3 mm Hg of carbon monoxide had been diluted to the atmospheric pressure with the ammonia-hydrogen mixture 1: 3 (stop cocks 14, 15 and 19 being held closed).

The progress of poisoning and recovering were also studied by measuring the decomposition rate every ten minutes. These processes went on also similary on both powders (Fig. 3b). It is to be noted that the activity of A (and AB) powder is somewhat greater after recovering than before poisoning.

The Effect of Thermal Treatment.—After the activities of new samples of catalyst No. 4 were determined at temperatures between about 400 and 500°C using the gas mixture 30:70 (Fig. 4), the temperature was raised to about 740°C and kept for one hour in the hydrogen stream. No change in activity was observed on the next day. The catalysts were further heated at about 830°C for one hour. The powder now showed a lower activity at the beginning of the measurement, but later recovered the activity to the value before the heat treatment. B showed, however, less activity throughout the whole measurement.

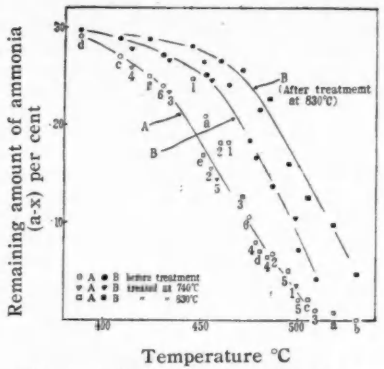

Fig. 4. Effect of heat treatment.

It seems that reduction at temperatures ranging from 300 to 520°C has caused a considerable grain growth of iron, and the heating at 740°C after the reduction does not effect any further change in the surface structure. The decrease in activity of B powder heated at 830°C may be considered, apart from the effect of simple sintering, in conjunction with our previous ion-microscopical observation that potassium in B powder above 800°C migrates through grain boundaries and evaporates from the surface.

The Effect of Mixing B Powder to the Catalyst Singly Promoted with Alumina.—As reported previously A and B powders

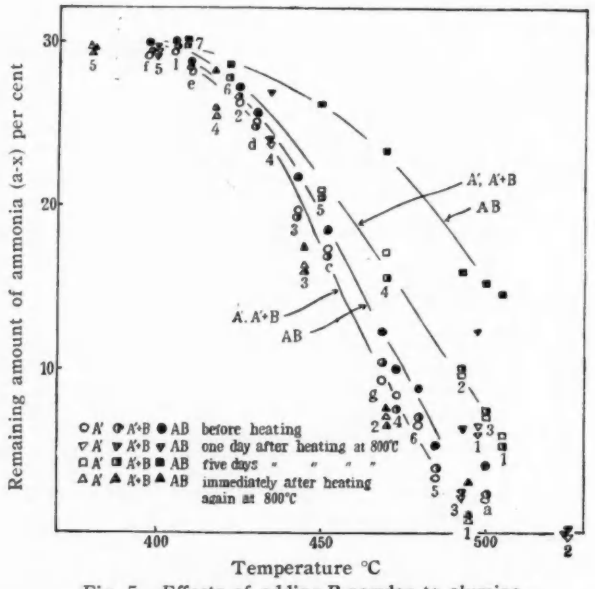

Fig. 5. Effects of adding B powder to alumina-promoted catalyst.

contain about 0.4 and 4 per cent of potash respectively. If potassium at the temperature of ammonia synthesis could now migrate from B powder to A powder, which has in some way lost potassium, B powder could play the role of potash source and contribute to the maintenance of activity of the catalyst. The idea was tested by the possible change in activity toward the ammonia decomposition of an alumina-promoted catalyst (A'), in which a small amount of B powder had been added before reduction.

The samples filled in the three tubes were respectively

(A') catalyst No. 2 (promoter: 5% Al_2O_3)

(A'+B) mixture of 97 parts of catalyst No. 2 and 3 parts of B powder from catalyst No. 4

(AB) catalyst No. 4 (promoters: 5% Al_2O_3 and 1% K_2O)

The result is that A' and A'+B are almost equally and AB somewhat less active (Fig. 5). They were then heated for one hour at 800°C. On the following day A' and A'+B were found to be as active as before the heating (though they showed lower activities at the beginning of measurement), while AB showed somewhat less active (Fig. 5). If left for five days after reduction both A' and A'+B showed similar decreases in activity, and AB a greater decrease. These catalysts were again subjected to the same heat treatment and their activities were immediately measured. They were found to be rather greater than before the first heat treatment. As to the mechanisms of the recovery of activity during the decomposition tests and the diminution of activity during preservation at room temperature, various explanations are possible, but none of them has yet been tested experimentally.

In any case we may conclude that potassium in B grains probably does not play any important role in the commercial synthesis of ammonia.

Summary

An unreduced iron synthetic ammonia catalyst promoted with potash or potash and alumina was separated into two different sorts of powders (A and B). Some of their properties were mentioned in the previous reports. Their catalytic activities for decomposing ammonia mixed with hydrogen were studied at atmospheric pressure by a specially devised flow method. The results are:

1. Between about 400°C and 500°C and for the gas mixtures of several compositions, A powder is more active than B.

2. The actions of the gas mixture laden with water vapour over ice kept in a -7°C bath and of that with 0.4% carbon monoxide are much the same in the rate and extent of poisoning as well as in the rate of recovering when the admixing of the poisoning gases is discontinued. As to the liability to the effects, one sort of powder scarcely differs from another.

3. Heating at 740°C for one hour has no effect. Heating at 830°C for one hour makes B powder less active and A powder also less active at first, but its activity before heating is soon recovered in the course of a run.

4. The activity of a potash-free alumina-promoted catalyst is not affected by adding before reduction a small amount of potash-rich B powder.

I should like to express my sincere thanks to Professor Nobuji Sasaki for his kind guidance throughout this work.

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A Physico-chemical Study on the Hydrolysis of Thorium Nitrate

By Kuan PAN and Tong Ming HSEU

(Received July 14, 1954)

It has been known that all tetrapositive ions exhibit strong tendencies toward polymerization accompanied by hydrolysis. The hydrolysis and polymerization of zirconium in perchloric acid solution has been investigated by Connick and his coworkers[1,2] and it has been shown that in 2 M perchloric acid at 25°C the average zirconium species at low zirconium concentration has a charge somewhere between +3 and +4, corresponding to a mixture of Zr^{+4} and $ZrOH^{+3}$ or possibly ZrO^{2+}. It has also been known that thorium salts produce acidic solution and that gelatinous thorium hydroxide is precipitated from an old aqueous solution of thorium nitrate. Qualitatively, however, thorium salts exhibit a less marked tendency to hydrolyze in aqueous solution than zirconium, and little quantitative investigation has been found in previous literatures*[3]. The purpose of the present work is to study the hydrolysis of thorium nitrate in a very dilute solution and in the presence of sodium perchlorate which has been used for maintaining the solution at constant ionic strength by means of the pH measurement with glass electrode. The assumption is that in the presence of sodium perchlorate, there is no complicating effect such as polymerization and colloid formation except in the case of hydrolytic behavior. For purposes of calculation, the data are treated as though the activity coefficients of all ion species are equal to unity in a very dilute solution, or remain constant at constant ionic strength. The equilibrium constants of thorium ion species are calculated stoichiometrically from the data of hydronium ion concentration observed and the total concentration of thorium nitrate.

Experimental

A) **Materials.**—Conductivity water with a specific conductivity of 1.6 to 2.4×10^{-6} mho was used throughout this experiment.

Thorium nitrate of C. P. grade was purified by the hydrogen peroxide method[4] and then by the hexamine method[5]. The washed hydroxide was digested in sufficient nitric acid, and evaporated to dryness after each of repeated additions of water to remove the excess of acid. The hydrate of thorium nitrate was obtained by recrystallization. The stock solution of thorium nitrate was prepared directly by dissolving the salt in conductivity water free from carbon dioxide. The concentration of the stock solution was checked by the gravimetric method before use.

B) **Procedure and Apparatus.**—Solutions with the initial concentration of 10^{-2} mol. of thorium nitrate were made to be 0.05, 0.1, 0.3 and 0.5 M with respect to sodium perchlorate, respectively. Each solution was diluted successively with an equal volume of the sodium perchlorate solution of the specified concentration, so that the concentration of thorium nitrate was diluted to one half while the solution was kept practically at constant ionic strength.

The change in pH during the dilution was followed with a vacuum tube potentiometer, constructed in our laboratory as shown in one of the previous papers[6]. The glass electrode made by Beckman Instrument Inc., in U.S.A., and a vacuum tube, UX-54 A, made by Matsuda Co. in Japan were used in the potentiometer circuit.

The glass electrode was frequently calibrated against a series of pH buffer solutions. The pH measurement was carried out in an oil thermostat controlled at 25°±0.1°C. Approximately ten-minute intervals were allowed for the attainment of equilibrium in each measurement.

Result and Discussion

When thorium nitrate dissolves in a dilute solution and in the presence of sodium perchlorate which is used for maintaining the solution at constant ionic strength, it may be assumed that the pH value of the solution is governed by no complicating effect, but the hydrolytic behavior for which the following reactions involving thorium ion species may be supposed:

$$Th^{+4}+H_2O \rightleftarrows Th(OH)^{+3}+H^+,\ K_1 \quad (1)$$

$$Th^{+4}+2H_2O \rightleftarrows Th(OH)_2^{+2}+2H^+,\ K_2 \quad (2)$$

$$\cdots\cdots$$

$$Th^{+4}+nH_2O \rightleftarrows Th(OH)_n^{4-n}+nH^+,\ K_n. \quad (3)$$

* There are some reports on this problem, e.g., K. A. Kraus and R. W. Holmberg, U.S. Atomic Energy Commission Report (1950), which are not available to us.

1) Robert E. Connick and William H. McVey, *J. Am. Chem. Soc.*, **71**, 3182 (1949).

2) Robert E. Connick and William H. Reas, ibid., 73, 1171 (1951).

3) R. Schaal and J. Faucherre, *Bull. soc. chim. France*, **1947**, 927.

4) Arthur C. Neish, *J. Am. Chem. Soc.*, **26**, 781, (1904).

5) H. H. Willard and L. Gordon, *Anal. Chem.*, 26, 165 (1948).

6) K. Pan and T. M. Hseu, This Bulletin, **26**, 126 (1953).

Then if the most possible type of reaction among them is the n-th type, the hydrolysis constant, K_n, may be given by the following equation:

$$K_n=\frac{a_X\cdot a_H}{a_{Th}}=\frac{f_X f_H{}^n}{f_{Th}}\cdot\frac{C_X\cdot C_H{}^n}{C_{Th}}, \quad (4)$$

where a_{Th}, a_X, a_H; f_{Th}, f_X, f_H and C_{Th}, C_X, C_H are the activities, activity coefficients and concentrations of ion species, Th^{+4}, $Th(OH)_n{}^{+4-n}$ and H^+, respectively.

Then if the degree of hydrolysis is small, as a first approximation, equation (4) may be expressed as follows:

$$K_n\fallingdotseq\frac{f_X\cdot f_H{}^n}{f_{Th}}\frac{C_H{}^{n+1}}{nC} \quad (5)$$

$$\fallingdotseq K_f\frac{a_H{}^{n+1}}{nC}, \quad (6)$$

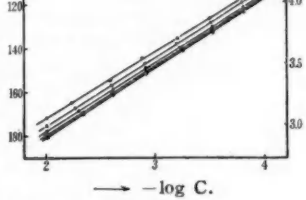
where C is the total concentration of the salt and $K_f=\frac{f_X}{f_{Th}\cdot f_H}$ is a constant at a constant ionic strength, consequently,

$$pH=\frac{1}{n+1}[pK_n-pK_f-\log n]-\frac{1}{n+1}\log C \quad (7)$$

$$=K-\frac{1}{n+1}\log C, \quad (8)$$

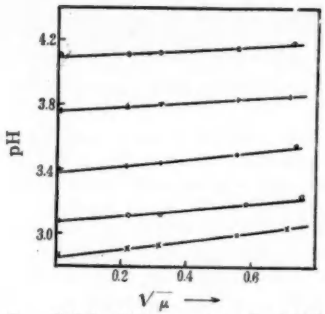
that is to say, a linear relation may be held between pH and $-\log C$, and the differential quotient of pH with respect to $-\log C$ is $\frac{1}{n+1}$.

As shown in Fig. 1, the curves plotting pH vs. $-\log C$ from 0.01 to 0.0001 M of thorium nitrate in sodium perchlorate solution as well as in pure water run parallel with each other and the slope is nearly equal to 1/2, that is, $n=1$, one may pressume that the existence of the ion, $Th(OH)^{+3}$ is highly probable. The linear relationship between the square root of ionic strength and pH at each concentration is indicated in Fig. 2.



×: in pure water
○: in 0.05M $NaClO_4$ soln.
●: in 0.1M $NaClO_4$ soln.
△: in 0.3M $NaClO_4$ soln.
○: in 0.5M $NaClO_4$ soln.

Fig. 1.



○: C 7.8×10^{-3} △: C $=3.125\times10^{-4}$
●: 1.25×10^{-3} □: 5.00×10^{-3}
×: 1.00×10^{-2}

Fig. 2.

In fact, since the hydrogen ion concentration in thorium nitrate solution is not so low as to be negligible against the total concentration of the salt, the above calculation is nothing but an approximate estimation. It suggests, however, that the average thorium ion species at this concentration range has a charge between +4 and +3 or even possibly +2, corresponding to a mixture of Th^{+4}, $Th(OH)^{+3}$ and $Th(OH)_2{}^{+2}$ or possibly ThO^{+2}.

For the purposes of calculating the equilibrium constants the data are treated as though the activity coefficients of all species in solution remain strictly constant at constant ionic strength and the general equilibrium constant is stoichiometrically expressed as

$$K_n=\frac{[Th(OH)_n{}^{4-n}]\ [H^+]^n}{[Th^{+4}]}. \quad (9)$$

Thus by expressing the total concentration of thorium and hydronium ion in a solution as a function of the equilibrium constants of all ion species as shown by the following stoichiometric relations,

$$[Th]_t=[Th^{+4}]+[Th(OH)^{+3}]+[Th(OH)_2{}^{+2}]\cdots\cdots$$

$$=[Th^{+4}]\left\{1+\frac{K_1}{[H^+]}+\frac{K_2}{[H^+]^2}\cdots\cdots\right\}$$

$$=[Th^{+4}]\left\{1+\sum_n\frac{K_n}{[H^+]^n}\right\} \quad (10)$$

and

$$[H^+]=[Th(OH)^{+3}+2[Th(OH)_2{}^{+2}]$$

$$+3[Th(OH)_3{}^{+1}]\cdots\cdots=[Th^{+4}]\left\{\frac{K_1}{(H^+)}+\right.$$

$$\left.\frac{K_2}{[H^+]^2}+\cdots\cdots\right\}=[Th^{+4}]\sum_n n\frac{K_n}{[H^+]^n}. \quad (11)$$

The stoichiometric ratio, r, of the hydronium ion concentration and the total concentration of thorium in the solution is expressed as follows:

$$r=\frac{[H^+]}{[Th]_t}=\frac{\sum_n K_n/[H^+]^n}{1+\sum K_n/[H^+]^n}, \qquad (12)$$

where $[Th]_t$ is the total concentration of thorium.

An attempt has been made to apply the experimental data to equation (12) for calculating the equilibrium constants of four ion species of $Th(OH)_n^{4-n}$, where n takes all the values of 1. 2, 3 and 4, using the least square method, but two negative values are obtained for two of the four constants which indicates the inadequacy of the application.

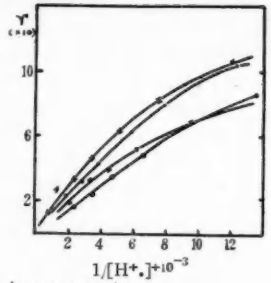
On the other hand, by assuming the existence of the ion species of Th^{+4}, $Th(OH)^{+3}$ and $Th(OH)_2^{+2}$ in the same solution of the specified condition as suggested by the above approximate estimation, and applying the same data to equation (12) to calculate the equilibrium constants, reasonable values of K_1 and K_2 for reactions (1) and (2) are obtained by the same method, as shown in Table I. Experimental values of r are plotted against $\frac{1}{[H^+]}$ at varying ionic strengths in Fig. 3.

TABLE I

CONCENTRATION EQUILIBRIUM CONSTANTS AT VARYING IONIC STRENGTHS AT 25°C

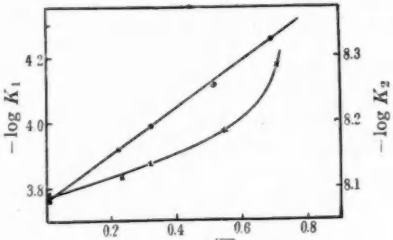
Ionic strength (In $NaClO_4$ solutions)	$K_1(\times 10^4)$	$K_2(\times 10^9)$
0.5 M	0.55	5.2
0.3 M	0.76	6.5
0.1 M	1.0	7.3
0.05 M	1.2	7.7
0	1.3	8.2
In pure water	1.7	8.2

The dissociation constants expressed as concentration equilibrium constants are strictly valid, however, only for solutions at constant ionic strength. The limiting values of K_1 and K_2 obtained by plotting K_1 and K_2 against $\sqrt{\mu}$ in Fig. 4, and extrapolating to zero ionic strength are 1.3×10^{-4} and 8.2×10^{-9}, respectively.



×: in pure water
●: in 0.1M $NaClO_4$ soln.
△: in 0.3M $NaClO_4$ soln.
○: in 0.5M $NaClO_4$ soln.

Fig. 3.



●: K_1 ×: K_2

Fig. 4.

Summary

1) The dilution effect on the pH change in a dilute solution and in the presence of sodium perchlorate was followed by a glass electrode.

2) A linear relationship is held between pH and $-\log C$. The curves plotting pH vs. $-\log C$ run parallel with each other at varying ionic strengths, and the slope is nearly equal to 1/2 by which the most possible existence of $Th(OH)^{+3}$ is pressumed.

3) The equilibrium constants for ion species, $ThOH^{+3}$ and $Th(OH)_2^{+2}$, are calculated stoichiometrically from the data of hydronium ion concentration observed and the total concentration of thorium nitrate.

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Dipole Moments of 2,3-Dihalogeno-2,3-dimethylbutanes

By Yonezo MORINO, Ichiro MIYAGAWA, Toshio HAGA, and San-ichiro MIZUSHIMA

(Received September 8, 1954)

Introduction

It has been shown by the measurements of the Raman effect, infrared spectra, dipole moment, etc., that 1,2-dihalogenoethanes[1,2] and simple hydrocarbons[2] are the equilibrium mixtures of the rotational isomers. However, 2,3-dibromo-2,3-dimethylbutane has been concluded by the spectoscopic investigation by Cleveland and Lamport[3] to have only one isomer (the *trans* isomer with center of symmetry in benzene and in carbon tetrachloride solutions). On the other hand van Arkel and Snoeck[4] reported a fairly large value 1.35 D of the dipole moment of 2,3-dichloro-2,3-dimethylbutane in benzene solution in spite of the vanishing moment in carbon tetrachloride solution. According to this result we have to assume the existence of both the *trans* and gauche forms in benzene solution, whereas we assume only the *trans* form with no moment in carbon tetrachloride solution. This does not seem to be compatible with our conclusions on rotational isomerism. At least, such a large solvent effect as that found by van Arkel and Snoeck will not be expected. In view of this situation it is desirable to measure the dipole moments of these substances more accurately in various solvents and at different temperatures.

Experimental

$Cl(CH_3)_2C\text{-}C(CH_3)_2Cl$.—Pinacon was treated with aqueous solution of hydrochloric acid saturated at −20°C, and the reaction product was allowed to stand for several days. The precipitate was recrystalized with ethyl ether and purified by sublimation: m.p. 155–156°C.

$Br(CH_3)_2C\text{-}C(CH_3)_2$.—The sample was supplied by Professor Cleveland, Illinois Institute of Technology. It is the same sample as that used by him and Lamport for the measurement of the Raman and infrared spectra. It was recrystalized from the solution and purified by sublimation: m.p. 157.4–158.5°C.

Benzene.—The commercial product was boiled with aluminium chloride for one hour, treated with concentrated sulphuric acid several times, dried over sodium, and then fractionally distilled: b.p. 80.0–80.5°C.

Carbon Tetrachloride.—The commercial product was dried over calcium chloride and then fractionally distilled: b.p. 75.6–75.9°C.

The apparatus and the method of the measurement of dielectric constant were already described in a previous paper[5]. The density of the solution at 25°C was measured with a pycnometer, and those at other temperatures were obtained by measuring the volume change of the solutions by use of a dilatometer.

Results

The observed values of dielectric constant ε and the density d of these substances in carbon tetrachloride and benzene solutions are shown in Tables I and II, where w is the

TABLE I

DIELECTRIC CONSTANT, DENSITY, AND MOLECULAR POLARISATION OF 2,3-DICHLORO-2,3-DIMETHYLBUTANE

($P_E+P_A=MR_D=39.66$ cc.).

Benzene Solution (25°C).

w	ε	d
0.00000	2.2720	0.8721
0.01439	2.3023	0.8755
0.02365	2.3198	0.8767
0.04225	2.3561	0.8797
0.06983	2.4089	0.8835
0.09048	2.4512	0.8865

$\varepsilon_\infty=2.2740$, $d_\infty=0.8734$,

$a=1.945$, $b=0.145$, $P_{2\infty}=101.0\pm0.4$ cc.

Carbon Tetrachloride Solution (−20°C).

w	ε	d
0.00000	2.3109	1.6770
0.01053	2.3344	1.6677
0.01428	2.3426	1.6644
0.02134	2.3584	1.6582
0.02650	2.3700	1.6537

$\varepsilon_\infty=2.3111$, $d_\infty=1.6771$,

$a=2.23$, $b=0.880$, $P_{2\infty}=76.4$ cc.

1) S. Mizushima, Y. Morino, I. Watanabe, T. Shimanouchi, and S. Yamaguchi, *J. Chem. Phys.*, **17**, 591 (1949).

2) S. Mizushima, "Structure of Molecules and Internal Rotation", Academic Press Inc., New York (1954).

3) F. F. Cleveland and J. E. Lamport, *J. Chem. Phys.*, **18**, 1320 (1950).

4) A. E. van Arkel and J. L. Snoeck, *Z. Physik. Chem.*, **B18**, 159 (1932).

5) Y. Morino, I. Miyagawa, and T. Oiwa, *Botyu-Kagaku*, **15**, 181 (1950).

(0°C).

0.00000	2.2722	1.6346
0.01053	2.2954	1.6257
0.01428	2.3037	1.6226
0.02134	2.3192	1.6167
0.02650	2.3301	1.6123

$\varepsilon_\infty=2.2720$, $d_\infty=1.6346$,
$a=2.20$, $b=0.840$, $P_{2\infty}=77.2$ cc.

(25°C).

0.00000	2.2254	1.5840
0.01053	2.2480	1.5757
0.01428	2.2557	1.5727
0.02134	2.2710	1.5671
0.02650	2.2821	1.5630

$\varepsilon_\infty=2.2252$, $d_\infty=1.5840$,
$a=2.14$, $b=0.791$, $P_{2\infty}=77.8$ cc.

(55°C).

0.00000	2.1651	1.5270
0.01053	2.1872	1.5189
0.01428	2.1954	1.5160
0.02134	2.2098	1.5105
0.02650	2.2206	1.5066

$\varepsilon_\infty=2.1653$, $d_\infty=1.5270$,
$a=2.10$, $b=0.771$, $P_{2\infty}=79.8$ cc.

TABLE II

DIELECTRIC CONSTANT, DENSITY, AND MOLECULAR POLARISATION OF 2,3-DIBROMO-2,3-DIMETHYLBUTANE

($P_E+P_A=MR_D=45.46$ cc.).

Benzene Solution (25°C).

0.00000	2.2720	0.8721
0.01529	2.2830	0.8785
0.01929	2.2858	0.8801
0.02903	2.2926	0.8841
0.03837	2.2987	0.8876

$\varepsilon_\infty=2.2729$, $d_\infty=0.8725$,
$a=0.679$, $b=0.454$, $P_{2\infty}=76.6\pm0.4$ cc.

Carbon Tetrachloride Solution (-15°C).

0.00000	2.3032	1.6662
0.00828	2.3102	1.6659
0.01100	2.3124	1.6664
0.01591	2.3170	1.6658
0.02046	2.3202	1.6665

$\varepsilon_\infty=2.3032$, $d_\infty=1.6662$,
$a=0.84$, $b=0$, $P_{2\infty}=63.7$ cc.

(+6°C).

0.00000	2.2622	1.6224
0.00828	2.2692	1.6221
0.01100	2.2716	1.6225
0.01591	2.2762	1.6220
0.02046	2.2800	1.6224

$\varepsilon_\infty=2.2620$, $d_\infty=1.6223$,
$a=0.86$, $b=0$, $P_{2\infty}=65.9$ cc.

(25°C).

0.00000	2.2259	1.5849
0.00828	2.2332	1.5847
0.01100	2.2354	1.5851
0.01591	2.2398	1.5845
0.02046	2.2450	1.5851

$\varepsilon_\infty=2.2261$, $d_\infty=1.5849$,
$a=0.86$, $b=0$, $P_{2\infty}=67.1$ cc.

(55°C).

0.00000	2.1640	1.5259
0.00828	2.1714	1.5255
0.01100	2.1740	1.5259
0.01591	2.1788	1.5257
0.02046	2.1831	1.5261

$\varepsilon_\infty=2.1640$, $d_\infty=1,5258$,
$a=0.91$, $b=0$, $P_{2\infty}=69.8$ cc.

concentration of the solute in weight fraction. The molecular polarisation $p_{2\infty}$ of the solute extrapolated to infinite dilution was calculated by use of the Halverstadt and Kumler equation[6]:

$$p_{2\infty}=(\varepsilon_0-1)/(\varepsilon_0+2)\cdot M_2/d_0\cdot \{1+3a/(\varepsilon_0-1)(\varepsilon_0+2)-b/d_0\}, \quad (1)$$

where M_2 denotes the molecular weight of the solute, ε_0 and d_0 the dielectric constant and the density extrapolated to zero concentration, and a and b the inclination of the lines of ε vs. w and d vs. w respectively. The dipole moment was calculated by the Debye equation:

$$\mu=0.0128\{p_{2\infty}-(p_E+p_A)\}^{1/2}T^{1/2} \quad (2)$$

where p_E and p_A are the electronic and atomic polarisations. p_E+p_A was assumed to be equal to MR_D, which was calculated from the atomic refractions of the constituent atoms. It is easily seen that this approximation does not affect our conclusion on the temperature dependence of dipole moment.

Discussion of Results

1. Rotational Isomers.—In the present experiment finite moments were observed for 2,3-dichloro-2,3-dimethylbutane in carbon tetrachloride solution as well as in benzene solution, in contrast to the result obtained by van Arkel and Snoek. This was also shown to be the case for 2,3-dibromo-2,3-dimethylbutane. Our results are shown in Table III, in which the experimental data in heptane solution obtained previously by one of us[7] are also included.

6) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem Soc.*, **64**, 2988 (1942).
7) I. Miyagawa, *J. Chem, Soc. Japan*, **75**, 1162 (1954).

TABLE III

DIPOLE MOMENTS OF 2,3-DICHLORO- AND 2, 3-DIBROMO-2, 3-DIMETHYLBUTANE IN VARIOUS SOLUTIONS (D)

°C	Chloro-compound			Bromo-compound		
	B[a]	CT[b]	Hp[c]	B[a]	CT[b]	Hp[c]
−20		1.24	1.14			0.77
−15					0.88	
0		1.30				
1			1.23			0.84
6					0.97	
25	1.74	1.37	1.31	1.24*	1.03*	0.96
50			1.41			1.02
55		1.47			1.15	

a) Benzene solution,
b) Carbon tetrachloride solution,
c) Heptane solution[7].
* The values referred to by Cleveland and Lamport[3], 1.20 and 1.01 D, in B and CT solution respectively, should be corrected as shown in the Table. The difference between the values of Cleveland and Lamport and of us comes from whether P_E+P_A is taken as MR_D or as 1.05 MR_D (the former).

The result obtained by Cleveland and Lamport on the Raman and infrared spectra of dibromodimethylbutane was explained by the existence of the *trans* form only, and therefore, was in apparent agreement with van Arkel's result of vanishing moment of dichlorodimethylbutane in carbon tetrachloride solution. Actually, however, there is a difficulty in this explanation, since the finite moment was observed in benzene solution and no difference in Raman spectra have been detected between benzene and carbon tetrachloride solutions. Thus van Arkel's result is not consistent with that obtaind by Cleveland and Lamport.

The dipole moment of the rigid *trans* form is evidently zero, and even if the rotational vibration about the trans position is taken into account, the moment value will not exceed 0.3 D (see Appendix). Therefore, we have to conclude the existence of a rotational isomer with a finite moment. This should be the less stable isomer, since the apparent moments of these compounds increase with temperature. From the analogy to 1,2-dihalogenoethanes this isomer can reasonably be assumed to be the gauche form, which is obtained from the *trans* form by an internal rotation by about 120°C.

The values of the dipole moment observed at a fixed temperature depend considerably upon the solvent as shown in Table III. In particular, the values observed in benzene solutions are much higher than those in other solutions. This result is quite analogous to that obtained for 1,2-dihalogenoethanes and many other compounds showing rotational isomerism[2] and is a further evidence of the existence of rotational isomers for dichloro- and dibromo-dimethylbutanes.

Let the number of the *trans* molecules be N_t and that of the gauche molecules be N_g. Then we have:

$$N_g/N_t=2(\mathcal{Q}_V{}^g\mathcal{Q}_R{}^g\mathcal{Q}_{int}{}^g)/(\mathcal{Q}_V{}^t\mathcal{Q}_R{}^t\mathcal{Q}_{int}{}^t)\cdot \exp(-\Delta E/kT), \quad (3)$$

where $\mathcal{Q}_{int}$ is the partition function for the internal rotation about the C−C axis, $\mathcal{Q}_V$ and $\mathcal{Q}_R$ the vibrational and rotational partition functions (excluding the internal rotation), and ΔE the energy difference of the two isomers. For the vibrational and rotational partition functions Gwinn and Pitzer[8] have shown the approximate relation:

$$\mathcal{Q}_V{}^g\mathcal{Q}_R{}^g/\mathcal{Q}_V{}^t\mathcal{Q}_R{}^t=1. \quad (4)$$

Therefore, we may assume the same relation for dichloro- and dibromo-dimethylbutane and can avoid the difficulty arising from the ambiguity of the assignment of the normal frequencies. If we assume further that $\mathcal{Q}_{int}{}^g/\mathcal{Q}_{int}{}^t=1$, eq. (3) is reduced to:

$$N_g/N_t=2\exp(-\Delta E/kT), \quad (5)$$

and the mean dipole moment is calculated as:

$$\bar{\mu}^2=(N_t\mu_t{}^2+N_g\mu_g{}^2)/(N_t+N_g) =\{\mu_t{}^2+2\mu_g{}^2\exp(-\Delta E/kT)\}/ \{1+2\exp(-\Delta E/kT)\}, \quad (6)$$

or

$$\bar{\mu}^2-\mu_t{}^2=(\mu_g{}^2-\mu_t{}^2)G(x), \quad (7)$$

where

$$G(x)=2\exp(-x)/\{1+2\exp(-x)\}, \quad (8)$$

and

$$x=\Delta E/kT. \quad (9)$$

The calculation of the energy difference ΔE and the moment μ_g of the gauche form from the mean moments observed at different temperatures is made according to the method proposed by Lennard-Jones and Pike[9].

First $G(x)$ is calculated for various values of $x=0\sim\infty$, and a curve is drawn for log $G(x)$ against log x. The experimental curve representing log $(\mu_{obs}{}^2-\mu_t{}^2)$plotted against log $1/T$ should be superposable on some part of the theoretical curve log $G(x)$ *vs.* log x. Hence, by shifting the experimental curve along x- and y-axes so as to superpose it on the $G(x)\sim$log (x) curve as much as possible, ΔE and $(\mu_g{}^2-\mu_t{}^2)$ are obtained from the displacements in x- and y-directions. In this treatment the value of μ_t should be known

8) W. D. Gwinn and K. S. Pitzer, *J. Chem. Phys.*, 16, 303 (1948).
9) J. E. Lennard-Jones and H. H. M. Pike, *Trans. Faraday Soc.*, 30, 830 (1934).

in advance. We have used two extreme values of μ_t, 0.0D and 0.3D, since as referred to above μ_t should be less than 0.3D.*

The results thus obtained are shown in Table IV, the estimated error in the value

TABLE IV

THE ENERGY DIFFERENCE BETWEEN THE ROTATIONAL ISOMERS OF DIHALOGENO-DIMETHYLBUTANE

Compound	Solvent	ΔE (kcal./mol.)	μ_t (D)	μ_g^{obs} (D)	μ_g^{calc} (D)
DCl	CT	1.10	0	2.8	3.33
		1.10	0.3	2.8	
	Hp	1.30	0	3.1	
		1.30	0.3	3.2	
DBr	CT	1.45	0	2.6	3.30
		1.60	0.3	2.6	
	Hp	1.50	0	2.6	
		1.50	0.3	2.6	

of the energy difference being $\pm$0.15 kcal/mol. It makes almost no difference, whether the value of μ_t be taken as 0.0D or as 0.3D. We see that there is dependence upon the solvent of the energy difference of dichlorodimethylbutane, although this is less pronounced than that observed for 1,2-dihalogenoethanes[10]. An explanation of the change of ΔE with solvent has been given in the case of 1,2-dihalogenoethanes[11,12]. In a medium of dielectric constant ε the gauche isomer is stabilized by an amount of energy $(\varepsilon-1)/(2\varepsilon+1)\cdot\mu^2/a^3$ as compared with the trans isomer, where a is the radius of the solute molecule. In other words the energy difference between the rotational isomers of dichloroethane decreases with the increasing polarity of the solvent. The same consideration would apply for dichlorodimethylbutane.

In contrast to the case of dichlorodimethylbutane, ΔE of the corresponding dibromo-compound was found to be almost independent of the solvent and, accordingly, ΔE in vacuum will also be 1.5 kcal./mol. In connection with this it may be noted that the change of ΔE of 1,2-dibromoethane with solvent was found by the earlier measurements[13,14,15] to be small as compared with dichloroethane. The accuracy of these measurements is not so high as in the case of those made recently, but they can be considered as experimental evidence in support of our conclusion on dichloro- and dibromo-dimethylbutanes.

In the earlier investigations on the internal rotation[2,13], the temperature dependence of dipole moment was explained on the assumption that the molecules exert rotatory vibration about the *trans* position which corresponds to the single minimum of the potential curve. The mean dipole moment was calculated by Lennard-Jones and Pike[9] as:

$$\bar{\mu}^2=2\mu_{2\perp}{}^2F(x), \tag{11}$$

where

$$F(x)=\int_0^{2\pi}(1-\cos\theta)\exp\{-x(1-\cos\theta)\}d\theta/\int_0^{2\pi}\exp\{-x(1-\cos\theta)\}d\theta, \tag{12}$$

and

$$x=V_0/2kT, \tag{13}$$

and

$$V=1/2\cdot V_0(1-\cos\theta). \tag{14}$$

Here $\mu_\perp$ is the component of the dipole moment of the rotating group perpendicular to the rotation axis. As shown by curve **a** of Fig. 1, the observed values of 1,2-dichloro

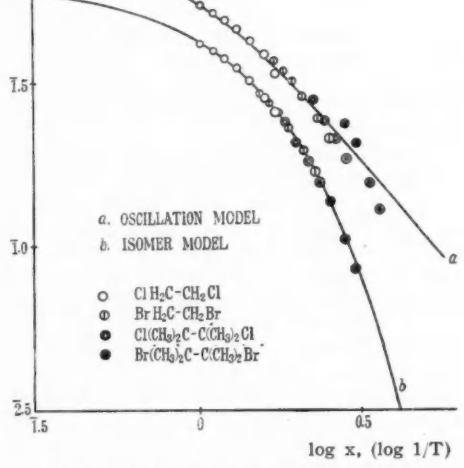


Fig. 1. The observed values of dipole moments and the computed values obtained on the assumption of the rotatory vibration about the *trans* position and on the assumption of the coexistence of two rotational isomers.

* Strictly speaking, the value of μ_g depends on temperature. However, as the temperature dependence can be shown to be small, we can safely use a constant value for μ_g.

10) Y. Morino, S. Mizushima, K. Kuratani, and M. Katayama, *J. Chem. Phys.*, **18**, 754 (1959).

11) I. Watanabe, S. Mizushima, and Y. Masiko, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **40**, 425 (1943): cf. P. J. Powling and H. J. Bernstein, *J. Am. Chem. Soc.*, **73**, 1815 (1951).

12) A. Wada, *J. Chem. Phys.*, **22**, 198 (1954).

13) S. Mizushima, Y. Morino, and K. Higasi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **25**, 159 (1934).

14) C. P. Smyth, R. W. Dornte, and E. B. Wilson, Jr., *J. Am. Chem. Soc.*, **53**, 4242 (1931).

15) G. I. M. Bloom and L. E. Sutton, *J. Chem. Soc.*, 727 (1941).

and 1,2-dibromo-ethane are in agreement with the computed values. Yet the observed values can also be brought into agreement with the theoretical curve computed from eq. (7) which was derived on the assumption of the coexistance of two rotational isomers (curve **b** in Fig. 1). Therefore, so far as the dipole moments of 1,2-dihalogenoethanes are concerned, we can not tell which of the two explanations is preferable, the vibration of two halves of molecules against each other in one potential trough or the coexistence of two rotational isomers.

However, in the case of 2,3-dibromo-2,3-dimethylbutane no displacement enables us to superpose the observed values on the theoretical curve **a** obtained on the assumption of the rotatory vibration about the *trans* position. Even in the chloro-compound there is a small but definite discrepancy between the experimental and theoretical curves. The difference in the two cases can be explained as a result of the lower potential barrier for 1,2-dichloro- and -dibromo-ethane and of the higher potential barrier for 2,3-dichloro- and -dibromo-2,3-dimethylbutane. It is quite reasonable to assume that dihalogenodimethylbutanes have barriers higher than dihalogenoethane since the van der Waals radius of methyl group is much larger than that of the hydrogen atom.

2. The Origin of the Energy Difference between the Rotational Isomers. — The nature of the hindering potential to internal rotation has been discussed by several investigators[16–19]. From the comparison of the many experimental data we have come to the conclusion that the stable positions of the internal rotation are determined mainly by the steric repulsion between the atoms of the rotating groups including hydrogen atoms, whereas in the energy difference between rotational isomers there are contributions of other intramolecular forces besides the steric repulsion[19].

As referred to above, the energy difference of 2,3-dibromo-2,3-dimethylbutane was found to be almost the same as that of 1,2-dibromoethane. This fact can not be understood, if the hindering potential arises only from the steric repulsion, since the repulsion arising from the CH_3 group may be considered to be almost the same as that from Br-atom. (As referred to above, the van der Waals radius of the bromine atom is of the same magnitude as that of the CH_3-group). In other words, if the energy difference would arise only from the steric repulsion, we should find the vanishing value of ΔE for dibromodimethylbutane, which is inconsistent with the experimental result. Therefore, we have to conclude that electrostatic forces should play an important part in ΔE. This is compatible with the fact that we have found almost the same value of ΔE for 2,3-dibromo-2,3-dimethylbutane and 1,2-dibromo-ethane, both of which are expected to have nearly the same electrostatic potential, since the dipole moments of the rotating groups are almost the same for both cases.

The same conclusion is derived for 2,3-dichloro-2,3-dimethyl-butane by comparing the value of ΔE (1.6kcal)** with that of 1,2-dichloroethane (1.2kcal). There is a small difference between these two values, but all we can say is that ΔE of the former substance is not smaller than that of the latter. We go too far, if we discuss this difference quantitatively.

We should like to refer to a recent paper by one of us (I. M.)[20], in which the configurations of the rotational isomers and the energy difference were discussed on the assumption that the steric repulsion between the rotating groups could approximately be calculated from the interatomic potentials obtainable from the experimental data on the second virial coefficients and the electrostatic energy from the interactions between the point dipoles located at each bond.

3. The Dipole Moment of the Gauche Form.—The dipole moment of the gauche form μ_g was found to be 3.1D for 2,3-dichloro-2,3-dimethylbutane and 2.6D for 2,3-dibromo-2,3-dimethylbutane (in heptane solution). These values are greater than those of 1,2-dichloro-(2.62D)[21] and 1,2-dibromo-ethane (2.23D)[21]. The greater values of the former two substances are considered to arise from the induction effect in the methyl radicals by the C-X dipoles. If the induction effect is calculated according to the empirical rule derived by two of us[22] the resultant moments of the gauche forms of 2,3-dichloro- and 2,3-dibromo-2,3-dimethylbutanes are found to be 3.33D and 3.30D respectively. The corresponding

16) E. N. Lassettre and L. B. Dean, *J. Chem. Phys.*, 17, 317 (1949).
17) H. J. Bernstein, *J. Chem. Phys.*, 17, 262 (1949).
18) L. J. Oesterhoff, *Discussion of the Faraday Soc.*, 10, 79 (1951).
19) S. Mizushima, Y. Morino, and T. Shimanouchi, *J. Phys. Chem.*, 56, 324 (1952).

** ΔE of 2,3-dichloro-2,3-dimethylbutane, 1.6 kcal., has been obtained by extrapolation to $\varepsilon=1$.

20) I. Miyagawa, *J. Chem. Soc. Japan*, 75, 1169, 1173, 1177 (1954).
21) I. Miyagawa, *J. Chem. Soc. Japan*, 75, 1057 (1954).
22) Y. Morino, I. Miyagawa and T. Oiwa, *Botyu-Kagaku*, 15, 181 (1950); I. Miyagawa, *J. Chem. Soc., Japan* 75, 1061 (1954).

experimental values 3.1D and 2.6D are somewhat less than the computed values. However, it should be noted that the experimental values of μ_g are obtained on the assumption that $S=Q_{int}{}^g/Q_{int}{}^t=1$. If different values are assigned to S, the values of μ_g become quite different from the above ones. If, for instance, S is taken as 1/2, μ_g will be 3.5D for dichloro- and 3.2D for dibromo-dimethylbutanes. It will be shown from the discussion of partition functions that S may be taken to be less than 1[23].

On the other hand the observed value of ΔE does not depend appreciably on the value of S and, therefore, as the experimental molecular constant of rotational isomers the energy difference ΔE is more reliable than μ_g.

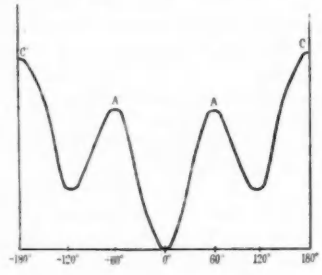
4. Molecular Spectra and Dipole Moments.—Let us now discuss the experimental result of Cleveland and Lamport. According to the Raman and infrared spectra observed by them in benzene and carbon tetrachloride solutions the molecules of 2,3-dibromo-2,3-dimethylbutane have been concluded to be in the *trans* form in both solutions. This seems at first sight to be inconsistent with the results of our dipole measurement. However, as the concentration of 2,3-dibromo-2,3-dimethylbutane in their measurement was considered to be less than 0.1 molar fraction and, as ΔE can reasonably be assumed to be 1.5 kcal./mol., the concentration of the gauche form is at most 0.014 in molar fraction. Even if the energy difference is reduced to half (ΔE=700 cal./mol.) the concentration of the gauche form would not exceed 0.02 in molar fraction. Therefore, it is no wonder that the bands arising from the gauche form were not observed.

In connection with this we should like to refer to the Raman spectra of 1,2-dibromoethane. The Raman line at 551 cm^{-1} assigned to the stretching frequency of the gauche form has a fairly strong intensity in the spectra of the pure liquid, but, when it is diluted with *n*-heptane, the intensity decreases more quickly than the line arising from the *trans* form, and finally at the molar fraction of 0.1 the line becomes too weak to be detectable[13]. The most intense line in the spectra of 2,3-dibromo-2,3-dimethylbutane would be the line arising from the corresponding C-Br stretching frequency, which will behave in the same manner as the 551 cm^{-1} line referred to above. Therefore, as the molar fraction of the dibromodimethylbutane solution in the experiment of Cleveland and Lamport was about 0.1 or less, it is quite possible that all the lines of the gauche form of dibromo-dimethylbutane escaped detection.

23) I. Miyagawa, *J. Chem. Soc. Japan*, **75**, 970 (1954).

Appendix

The hindering potential to internal rotation about the central C-C bond as axis is considered to have a form such as shown in Fig. 2. The



gauche trans gauche

Fig. 2.

more stable position corresponds to the *trans* form, and the less stable positions to the gauche forms which are obtained from the *trans* form by an internal rotation by about $\pm 120°$. There are two lower barriers A and A' and one higher barrier C in one complete internal rotation. Therefore, in order to obtain the moment of the *trans* isomer, μ_t, or, exactly speaking, the mean moment of all the molecules in the *trans* trough, we must make an integration:

$$\bar{\mu}_t{}^2=2\mu_\perp{}^2\int_{A'}^{A}(1-\cos\theta)\exp(-V(\theta)/kT)d\theta/\int_{A'}^{A}\exp(-V(\theta)/kT)d\theta, \quad \text{(A1)}$$

where $\mu_\perp$ is the perpendicular component of the moment of the rotating group. The potential function $V(\theta)$ in this expression may reasonably be approximated as:

$$V(\theta)=1/2\cdot V_0(1-\cos 3\theta), \quad \text{(A2)}$$

and, furthermore, the limit of integration A and A' in terms of azimuthal angle may be taken as $\pm 60°$. Then we have

$$\mu_t{}^2=2\mu_\perp{}^2F(x), \quad \text{(A3)}$$

where

$$F(x)=3\sqrt{3}/(2\pi I_0(x))\cdot\left[I_0(x)+2\sum_{\Delta=1}^{\infty}(-1)^\Delta/(9\Delta^2-1)\cdot I_\Delta(x)\right], \quad \text{(A4)}$$

and

$$x=V_0/2kT. \quad \text{(A5)}$$

Here $I_\Delta(x)$ denotes the modified Bessel function of the first kind. If the bond moment of C-Cl is

TABLE V

THE TABLE OF $F(x)$

x	$F(x)$
0	0.1730
0.5	0.1243
1	0.0812
2	0.0413
5	0.0125
10	0.0064

taken as 1.86D, and the induction effect of C-Cl moment upon the $C-CH_3$ bonds is calculated according to our empirical rule, the perpendicular component $\mu_\perp$ is obtained as 2.15D. Using this value, μ_t at 300°K is calculated as shown in Table VI. As the value of V_0 for hexachloroethane was

TABLE VI

THE CALCULATED MOMENT OF THE TRANS FORM AT 300°K

V_0 (kcal./mol.)	μ(D)
0	1.14
0.5	1.00
1	0.83
2	0.62
3	0.50
5	0.36
10	0.23

found to be about 10 kcal./mol., that of dichlorodimethylbutane must be greater than 10 kcal./mol., since the potential barrier arises mainly from the steric repulsion between the atoms of the rotating groups and is much higher in dichlorodimethylbutane than in hexachloroethane. (As referred to above the van der Waals radius of the methyl group is much larger than that of a Cl atom. In fact, the hindering potential barrier of 1,1,1-trichloroethane was found to be 2.7 kcal./mol.[24], while that of neopentane is 4.3 kcal./mol.[25], the latter being obtained by the replacement of chlorine atoms of the former by methyl radicals. Therefore, from Table V, we can surely conclude that μ_t is smaller than 0.3D.

The value of μ_t of 2,3-dibromo-2,3-dimethylbutane will be still smaller, since the steric repulsion in dibromo-compound should be much larger than that in dichloro-compound.

24) J. R. Lubin, B. H. Lebedahl, and D. M. Yost, *J. Am. Chem. Soc.*, **66**, 279 (1944).

25) K. S. Pitzer, *Discussion of the Faraday Soc.*, **10**, 66 (1951).

Summary

The dipole moments of 2,3-dichloro- and 2,3-dibromo-dimethylbutane were measured in carbon tetrachloride solution in the temperature range from −25° to +55°C, and in benzene solutions at 25°C. The moment was found to increase with temperature in carbon tetrachloride solution. Much higher values of moment were observed in benzene solutions. It was concluded from these experimental results that there exist two rotational isomers, the *trans* isomer with vanishing or a small moment, and the gauche isomer with a finite moment. The experimental result could be explained satisfactorily by the rotational isomer theory, but not on the assumption of only one potential trough at the *trans* position.

By comparing the energy difference between the rotational isomers of these compounds with those of 1,2-dichloro- and 1,2-dibromoethane it was concluded that the electrostatic force plays an important role in the energy difference between the rotational isomers, whereas the potential barrier is mainly determined by steric repulsion.

An explanation was presented to reconcile the result of our dipole measurement with that of Raman and infrared measurement, the two results being in apparent contradiction with each other.

The authors wish to thank Professor Forrest F. Cleveland, Illinois Institute of Technology, for sending us a sample of 2,3-dibromo-2,3-dimethylbutane and for his interest in our measurement.

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A Rapid Determination of Oxidation Values of Non-Volatile Organic Compounds by the Iodic Acid Decomposition Method

By Shigeru OHASHI

(Received September 27, 1954)

In the course of preparing organic compounds, on many occasions, it is only necessary to determine the percentages of carbon or other elements to serve as a check on the purity. For this purpose, however, it is not always necessary to determine the content of an element such as carbon, hydrogen, or nitrogen, but instead the "oxidation value" of the compound, named by the author, can also be useful. The oxidation value of a compound is defined as the number of oxygen atoms required to completely oxidize one molecule of the compound.

A survey of the literature reveals that Strebinger[1] and Christensen, Facer, and

1) R. Strebinger, *Z. analyt. Chem.*, **58**, 97 (1919).

Wong[2,3] determined the "oxygen consumed" of an organic compound, which is defined as oxygen requirement in gram per hundred grams of the sample, by means of iodic acid in concentrated sulfuric acid. In spite of all these developments there is still need for wider applicability, simpler techniques, less expensive equipment, and methods by which the occasional determination can be made easily.

For the complete wet combustion of organic compounds a powerful oxidizing agent is required and, furthermore, to determine the oxidation values of the compounds, the reduced part of the oxidant must be measured readily and exactly after the oxidation reaction. Iodic acid in strong phosphoric acid is a very suitable reagent for this purpose. The strong oxidizing action of this reagent was already used by the author and his co-workers[4] for the determination of elementary carbon, such as charcoal, graphite, and others, which are completely oxidized by it to form carbon dioxide.

$$5C+4HIO_3=5CO_2+2I_2+2H_2O$$

The amount of the reduced part of iodic acid can be known by means of a volumetric determination of the iodine produced.

Now one may suppose in general an organic compound composed of carbon, hydrogen, and oxygen, and indicate it as $C_kH_mO_n$. Then the oxidation of the organic compound with iodic acid is shown by the following equation (3), which is derived from equations (1) and (2).

$$C_kH_mO_n+(2k+m/2-n)\,O=k\,CO_2+m/2H_2O \quad (1)$$

$$2HIO_3=H_2O+I_2+5O \quad (2)$$

$$5C_kH_mO_n+2(2k+m/2-n)HIO_3 = 5kCO_2+(2k+3m-n)H_2O + (2k+m/2-n)I_2\,. \quad (3)$$

Namely, 5 mol. of the organic compound $C_kH_mO_n$ is oxidized completely with $2(2k+3m-n)$ mol. of iodic acid under the production of $(2k+m/2-n)$ mol. of iodine. Therefore, if the organic compound is completely oxidized with the reagent according to the above equation, its oxidation value may be obtained by the determination of the iodine produced.

In this study the method of determining the oxidation values based on the above-mentioned principle was investigated and the oxidation values were determined for several non-volatile organic compounds, which are composed of carbon, hydrogen, and oxygen.

Apparatus

The apparatus used in this study is illustrated in Fig. 1. It is mainly composed of two parts, a reaction vessel A and an absorption vessel B. The right tube of the vessel A is closed at the top by means of a rubber stopper R_1, through which a gas-introducing tube and a thermometer are inserted. The thermometer is protected by a glass tube. If the thermometer-protecting tube is not used, the very thin bottom glass of the thermometer may easily be destroyed by heating with strong phosphoric acid. In the right arm of the vessel A, there is a constricted part above which a small glass lock shown in Fig. 2 is set for the sake of protecting it against the backward stream of gas. The left arm of the vessel A is inserted deeply into the absorption vessel B through a rubber stopper R_2. In order to prevent the liberated iodine from going upward to the rubber stopper R_2, the right arm of the vessel B is constricted at the position as shown in Fig. 1. On the left arm of the vessel B, there is an outlet, having a short rubber tube and a pinch cock, for convenience to pour out the solution in the vessel. The top of the left arm is closed by

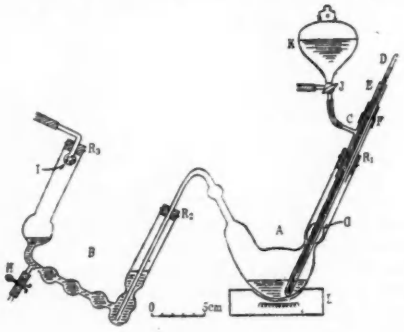

Fig. 1 Apparatus

A: Reaction vessel
B: Absorption vessel
C: Gas-introducing tube
D: Thermometer
E: Thermometer-protecting tube
F: Rubber tube
G: Glass lock
H: Pinch cock
I: Glass bulb
J: Three-way stopcock
K: Water-addition funnel
L: Electric heater
R_1-R_3: Rubber stopper

Fig. 2 Glass lock.

Fig. 3. Weighing tube.

2) B. E. Christensen and J. F. Facer, *J. Am. Chem. Soc.*, **61**, 3001 (1939).
3) B. E. Christensen and R. Wong, *Ind. Eng. Chem., Anal. Ed.*, **13**, 444 (1941).
4) T. Kiba, S. Ohashi, T. Takagi, and Y. Hirose, *Japan Analyst*, **2**, 446 (1953).

means of a rubber stopper R_3, through which a glass tube with a small glass bulb, having some pinholes, is inserted to prevent loss from a splash.

After passing through the solutions of sodium carbonate, potassium permanganate, and mercuric chloride in turn, the air is introduced by means of a suction pump into the vessel A through the three-way stopcock of a water-addition funnel, which is used to add water to the vessel A after the decomposition of a sample.

The vessel A is heated at the bottom with an electric heater, the temperature of which can be regulated with a transformer.

Reagents

Potassium Iodate.—Standard reagent grade (The Osaka Industrial Research Institute) or extra pure grade potassium iodate was used.

Strong Phosphoric Acid.—Commercial extra pure grade orthophosphoric acid (d=1.7) was dehydrated by heating until the temperature of the liquid reached 300°C. The very viscous liquid thus obtained is called strong phosphoric acid[5], which is a mixture of ortho-, pyro-, and triphosphoric acid.

Standard Solution of Sodium Arsenite.—A 0.1 N solution of sodium arsenite was used. Dissolve 4.95 g. of standard reagent grade (The Osaka Industrial Research Institute) arsenic trioxide in 150 ml. of 10% sodium carbonate solution, add 25 ml. of normal sulfuric acid, and dilute to 1000 ml.

Standard Solution of Iodine.—A 0.05 N solution of iodine was used. It was standardized with the above sodium arsenite solution.

Procedure

Weigh accurately a 15 to 100 mg. sample, depending upon its oxidation value, into a small weighing tube shown in Fig. 3; choose the sample weight so that the iodine formed will not consume more than 50% of the sodium arsenite used. From a buret, pour about 3 to 5 ml. of strong phosphoric acid into a reaction vessel A through its upper inlet, and add a suitable amount of powdered potassium iodate. The optimum amount of potassium iodate will be discussed later. Next, let fall the weighing tube containing the sample along the inside wall of the vessel carefully. Add 10 or 20 ml. of sodium arsenite solution into an absorption vessel B. If only 10 ml. of sodium arsenite solution is used, add further about 10 ml. of water. Then connect all of the vessel A, B and so on.

While a slow stream of washed air is flowing through the vessel A and B by a suction pump, gently heat the bottom of the vessel A on a small electric heater. With increase of temperature, viscosity of the reaction medium decreases and a decomposition reaction begins at the appearance of a violet vapor of iodine. During the decomposition reaction shake the vessel A in order to get a complete reaction.

The reaction temperatures are varied from 80° to 240°C in accordance with species of samples. However, the temperature of the reactants must be kept carefully under 260°C, because at any higher temperature than this limit iodic acid is decomposed with the evolution of iodine[6].

The end of the decomposition reaction is easily recognized by the ceasing of the production of iodine. After the end of the decomposition reaction, stand the vessel A aloof from the electric heater until the temperature of the reaction medium falls to about 140°C, while air is flowing through the vessel.

After the cooling, open the three-way stopcock and introduce 10 to 15 ml. of water into the vessel A. Then heat once more the aqueous solution in the vessel A on the electric heater, until all of the iodine dissolved in the reaction solution is removed and absorbed into the sodium arsenite solution.

Remove the absorption vessel B from the rubber stoppers, let the solution flow into a beaker, and wash out the vessel B and the small glass bulb with water. Add some sodium bicarbonate to the solution in the beaker and titrate the excess sodium arsenite with 0.05 N iodine solution using starch solution as indicator.

Results and Discussion

In order to estimate the indispensable quantity of potassium iodate for the complete oxidation of an organic compound, the following experiment was carried out in the case of oxalic acid as an example.

About 50 mg. of oxalic acid weighed accurately was oxidized with various amounts of potassium iodate and the iodine produced was measured by the procedure described above. Results obtained are given in Table I. Nos. 4 and 5 in this experiment have

Table I

Amount of potassium iodate required for complete oxidation of oxalic acid

No.	Sample Weight mg.	Potassium Iodate Used mg.	Potassium Iodate Ratio: mg. used to mg. equiv.	Iodine Produced Found mg.	Iodine Produced Ratio: mg. found to mg. calc.
1	51.5	20.5	0.58	11.6	0.56
2	50.0	30.5	0.98	18.7	0.92
3	50.7	32.7	0.95	17.9	0.88
4	49.2	34.0	1.02	18.2	0.92
5	50.6	40.0	1.16	19.8	0.90
6	51.1	52.2	1.50	20.4	0.99
7	50.0	65.3	1.91	20.1	0.99
8	49.8	100.5	2.97	20.1	1.00

indicated obviously that an amount of potassium iodate slightly in excess of that required theoretically can not oxidize the sample completely. For this purpose an excess of at least half as much again as the theoretical

5) L. F. Audrieth, "Inorganic Syntheses, Volume III", McGraw-Hill Book Company, Inc., New York, (1950), p. 89.

6) T. Kiba et al., loc. cit.

quantity should be used.

In the first course of this investigation the reactions were carried out in the stream of carbon dioxide, but if a sample and sodium arsenite solution can not be oxidized with air, air may be used instead of carbon dioxide. With regard to this presumption the following tests were performed.

At first in order to investigate the stability of sodium arsenite solution against aeration, the washed hot air accompanied with aqueous vapor was introduced into a certain amount of sodium arsenite solution at the rate of about 5 bubbles of air per second. After the aeration titrating the arsenite solution with the standard solution of iodine, the data shown in Table II were obtained. This result

TABLE II

EFFECT OF AERATION ON STABILITY OF SODIUM ARSENITE SOLUTION

Quantity of 0.05 N Iodine Solution Consumed	
Before Aeration ml.	After 1 hr. of Aeration ml.
34.43	34.44
34.43	34.44
8.89	8.88
8.89	8.88

shows that the sodium arsenite solution can not be oxidized by one hour's aeration. Since the period of aeration in the practical procedure is shorter than thirty minutes, the oxidation of the arsenite solution with air may be out of the question.

Next, for the determination of the oxidation value of sodium oxalate, for example, the air flowing method was compared with the carbon dioxide flowing method. As shown in Table III there is no difference between the two methods.

TABLE III

COMPARISON OF CARBON DIOXIDE FLOWING METHOD AND AIR FLOWING METHOD

Sample: Sodium Oxalate

Gas Used	Sample Weight	Iodine Produced		Deviation
		Calc.	Found	
	mg.	mg.	mg.	mg.
CO_2	33.2	12.5_8	12.5_2	-0.0_6
〃	50.0	18.9_4	18.9_2	-0.0_2
〃	82.5	31.2_5	31.1_5	-0.1_0
〃	87.5	33.1_5	33.0_6	-0.0_9
Air	30.5	11.5_5	11.5_1	-0.0_4
〃	57.0	21.5_9	21.5_5	-0.0_4
〃	45.3	17.1_6	17.1_1	-0.0_5
〃	80.9	30.6_4	30.3_9	-0.2_5

Analyses of some known organic compounds were carried out by this method. These results are summarized in Table IV. Purest

TABLE IV

DETERMINATION OF OXIDATION VALUES OF SOME COMPOUNDS BY THIS METHOD

Substance	Oxidation Value Calc.	Reaction Temperature °C	Sample Weight mg.	Iodine Produced		Oxidation Value	
				Calc. mg.	Found mg.	Found	Deviation from Average
Oxalic acid $H_2C_2O_4 \cdot 2H_2O$	1	90–120	34.6	13.9_3	13.9_4	1.00_1	-0.00_1
			42.8	17.2_4	17.3_3	1.00_5	$+0.00_3$
			53.2	21.4_2	21.4_4	1.00_1	-0.00_1
			60.4	24.3_2	24.3_3	1.00_0	-0.00_2
			73.2	29.4_8	29.6_1	1.00_4	$+0.00_2$
					Av.	1.00_2	
Sodium oxalate $Na_2C_2O_4$	1	80–150	34.7	13.1_4	13.2_1	1.00_5	-0.00_1
			41.6	15.7_6	15.7_6	1.00_4	-0.00_2
			55.9	21.1_7	21.3_2	1.00_7	$+0.00_1$
			78.4	29.7_0	29.9_0	1.00_7	$+0.00_1$
					Av.	1.00_6	
Tartaric acid $C_4H_6O_6$	5	80–150	25.4	42.9_5	42.9_7	5.00_5	$+0.01_1$
			26.5	44.8_0	45.0_7	5.01_5	$+0.02_1$
			33.9	57.3_2	57.2_1	4.99_0	-0.00_4
			35.9	60.7_1	60.0_0	4.94_0	-0.05_4
			40.4	68.3_4	68.3_7	5.00_5	$+0.01_1$
			45.3	76.6_0	76.5_6	4.99_5	$+0.00_1$
			55.7	94.1_9	94.4_2	5.01_0	$+0.01_6$
			64.9	109.8	109.5	4.98_5	-0.00_9
			75.0	126.8	126.8	5.00_0	$+0.00_6$
					Av.	4.99_4	

TABLE IV (Contd.)

Substance	Oxidation Value Calc.	Reaction Temperature °C	Sample Weight mg.	Iodine Produced		Oxidation Value	
				Calc. mg.	Found mg.	Found	Deviation from Average
Sodium potassium tartrate $C_4H_4O_6NaK \cdot 4H_2O$	5	90–150	25.4	22.8_4	22.7_9	4.99_0	$+0.00_5$
			32.0	28.7_8	28.6_4	4.97_5	-0.01_0
			35.3	31.7_5	31.6_5	4.98_5	0.00_0
			47.1	42.3_6	42.1_9	4.98_0	-0.00_5
			50.4	45.3_2	45.2_6	4.99_5	$+0.01_0$
			65.3	58.7_2	58.5_4	4.98_5	0.00_0
					Av.	4.98_5	
Citric acid $C_6H_8O_7 \cdot H_2O$	9	80–150	23.5	41.0_9	41.4_9	9.08_1	$+0.00_3$
			26.8	58.2_6	58.5_8	9.05_4	-0.02_4
			39.5	85.8_7	86.7_1	9.09_0	$+0.01_2$
			39.8	86.2_3	86.9_3	9.07_2	-0.00_6
			40.7	88.4_8	89.2_8	9.08_1	$+0.00_3$
			48.1	104.6	105.6	9.09_0	$+0.01_2$
					Av.	9.07_8	
Sodium citrate $C_6H_5O_7Na_3 \cdot 5.5H_2O$	9	90–150	24.1	30.8_2	30.9_2	9.03_6	$+0.04_7$
			32.2	41.1_8	41.2_6	9.01_8	$+0.02_9$
			39.9	51.0_3	50.8_1	8.96_4	-0.02_5
			54.8	70.0_8	69.7_2	8.95_5	-0.03_4
			62.0	79.3_0	79.1_2	8.98_8	-0.00_1
			75.7	96.8_2	96.5_7	8.97_3	-0.01_6
					Av.	8.98_9	
Succinic acid $C_4H_6O_4$	7	160–230	19.4	58.3_7	57.9_3	6.94_4	-0.01_4
			20.9	62.8_9	62.4_5	6.95_1	-0.00_7
			22.0	66.2_0	65.9_9	6.97_9	$+0.02_1$
			29.1	87.5_6	87.0_1	6.95_8	0.00_0
			44.2	133.0	132.1	6.95_1	-0.00_7
			54.3	163.4	162.6	6.96_5	$+0.00_7$
					Av.	6.95_8	
Arabinose $C_5H_{10}O_5$	10	90–230	19.8	66.1_9	66.3_5	10.0_2	$+0.0_2$
			30.0	100.3	100.3	10.0_0	0.0_0
			33.4	111.7	111.2	9.9_5	-0.0_5
			47.1	157.5	156.7	9.9_5	-0.0_5
			50.5	168.8	169.8	10.0_6	$+0.0_6$
					Av.	10.0_0	
Glucose $C_6H_{12}O_6$	12	80–250	26.6	88.9_2	88.9_1	12.0_0	$+0.0_6$
			35.9	110.6	110.0	11.9_4	0.0_0
			36.6	122.4	121.2	11.8_8	-0.0_6
			41.1	134.2	133.8	11.9_6	$+0.0_2$
			44.4	136.9	136.3	11.9_5	$+0.0_1$
			62.8	193.4	192.5	11.9_4	0.0_0
					Av.	11.9_4	
Galactose $C_6H_{12}O_6$	12	80–230	25.2	85.1_9	84.9_9	11.9_8	$+0.0_2$
			26.5	89.5_8	88.9_8	11.9_2	-0.0_4
			35.9	121.4	120.9	11.9_5	-0.0_1
			46.3	156.5	156.4	11.9_9	$+0.0_3$
			50.6	171.1	170.7	11.9_8	$+0.0_2$
					Av.	11.9_6	
Dulcitol $C_6H_{14}C_6$	13	90–200	25.6	92.7_4	92.3_0	12.9_3	-0.0_3
			30.5	110.5	110.2	12.9_5	-0.0_1
			39.0	141.3	141.3	13.0_0	$+0.0_4$
			41.9	151.8	151.4	12.9_5	-0.0_1
			45.1	163.4	162.8	12.9_5	-0.0_1
			52.6	190.6	190.4	12.9_9	$+0.0_3$
					Av.	12.9_6	

TABLE IV (Contd.)

Substance	Oxidation Value Cale.	Reaction Temperature C°	Sample Weight mg.	Iodine Produced		Oxidation Value	
				Cale. mg.	Found mg.	Found	Deviation from Average
Saccharose	24	100–230	16.9	60.1$_6$	59.5$_0$	23.7$_8$	−0.0$_3$
$C_{12}H_{22}O_{11}$			20.7	73.6$_9$	73.0$_7$	23.8$_1$	0.0$_0$
			29.0	103.$_2$	102.$_4$	23.8$_1$	0.0$_0$
			33.8	120.$_3$	119.$_5$	23.8$_3$	+0.0$_2$
			37.1	132.$_1$	130.$_9$	23.7$_8$	−0.0$_3$
			40.0	142.$_4$	141.$_4$	23.8$_3$	+0.0$_2$
					Av.	23.8$_1$	
Treharose	24	90–230	12.4	44.1$_3$	44.0$_3$	23.9$_5$	+0.0$_1$
$C_{12}H_{22}O_{11}$			14.7	52.3$_2$	52.0$_7$	23.8$_8$	−0.0$_3$
			15.3	54.4$_5$	54.2$_5$	23.9$_3$	−0.0$_1$
			16.1	57.3$_0$	57.2$_2$	23.9$_8$	+0.0$_4$
					Av.	23.9$_4$	

grade organic compounds were selected or prepared and dried in the calcium chloride or sulfuric acid desiccator before analysis.

The results listed for the various organic compounds in Table IV indicate that the precision of the data is within ±1%.

The constantly high value obtained for citric acid might be due to the loss of a part of the crystallization water. The slightly low values for succinic acid and saccharose led to the belief that these substances had not been completely dried prior to analysis.

Most of the analyses reported in Table IV were conducted according to the procedure described above and required only twenty to thirty minutes for one estimation.

This method can not be applied to volatile samples such as benzoic acid. For the development of this method to the volatile compounds the apparatus would have to be improved. The investigation of this point is a future problem.

Summary

A new method has been developed to permit accurate and rapid determination of oxidation values of organic compounds. The oxidation value of a compound can be readily obtained by determining the iodine produced from the reaction of the organic compound and potassium iodate in strong phosphoric acid. The iodine produced is absorbed into the sodium arsenite solution and the excess arsenite is titrated with the standard solution of iodine.

The apparatus and procedures for this method have been investigated. According to the data obtained on some pure non-volatile organic compounds, utilizing sample weights of 10 to 80 mg., it is indicated that this method is very accurate and an analysis can be accomplished as rapidly as in twenty to thirty minutes.

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A Rapid Determination of Nitrogen in Organic Compounds by the Iodic Acid Decomposition Method

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The applications of the characteristic behavior of iodic acid in strong phosphoric acid to chemical analysis have been investigated, and the volumetric methods of determining elementary carbon[1] such as charcoal, graphite etc. and determining oxidation values[2] of organic compounds have been already reported by the author and his coworkers. In the course of these studies it was found that nitrogen contained in organic substances can be easily determined by the iodic acid-strong phosphoric acid reagent. If an organic compound containing nitrogen is heated with iodic acid in strong phosphoric acid, the compound is decomposed and the nitrogen in it is liberated. Consequently, after the decomposition mentioned above, sending this nitrogen with carbon dioxide into an azotometer which is filled with potassium hydroxide solution, the nitrogen can be determined gas-volumetrically. This method is, so to speak, the wet Dumas method; namely, the combustion tube in the case of the Dumas method is replaced by the special reaction vessel in which samples are decomposed.

Apparatus.—The apparatus necessary in this method is shown in Fig. 1. It is mainly composed of three parts, reaction vessel A, azotometer B, and carbon dioxide generator C. All of these are hand-made in addition to a Kipp's apparatus for production of carbon dioxide.

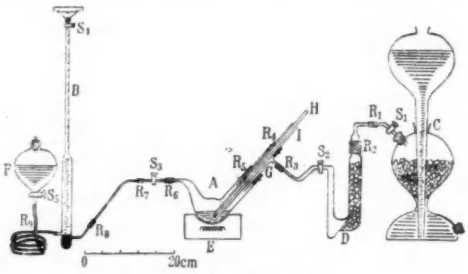

Fig. 1. Apparatus.

A: Reaction vessel.
B: Azotometer.
C: CO_2 generator.
D: $CaCO_3$-filled guard tube.
E: Electric heater.
F: Leveling vessel.
G: Gas-introducing. tube.
H: Thermometer.
I: Thermometer-protecting tube.
R_1-R_9: Rubber tube.
S_1-S_5: Stopcock.

Into the reaction vessel a gas-introducing tube G and a thermometer H, which is covered with a thermometer-protecting tube I, are inserted. These tubes are attached to the reaction vessel with suitable rubber tubes as shown in Fig. 1.

The measuring-tube of the azotometer is made of a commercial buret, which is graduated at intervals of 0.02 ml. and has a graduated capacity of 5 ml. It is connected at the bottom by means of a rubber tube with a leveling vessel F.

Between the reaction vessel and the Kipp's apparatus there is a calcium carbonate-filled guard tube D for catching particles of hydrochloric acid.

The reaction vessel is heated with an electric heater, the temperature of which is regulated with a transformer.

Reagents.—*Strong phosphoric acid.* Strong phosphoric acid prepared by heating and evaporating commercial extra pure grade orthophosphoric acid (d=1.7) until its temperature reached 300°C was used.

Potassium iodate.—Extra pure grade potassium iodate was used.

Carbon dioxide. This was produced from calcium carbonate (marble) and hydrochloric acid (1: 1) in a Kipp's apparatus. To obtain the carbon dioxide in the purest condition the operation of putting these substances into a Kipp's apparatus should be carried out in the same manner as that used in the case of the micro-Dumas method.

Potassium hydroxide. A 30% solution of potassium hydroxide was used.

Procedure.—Weigh accurately a 10 to 50 mg. sample, depending upon its nitrogen content, into a small weighing tube; choose the sample weight so that the volume of the nitrogen formed will be 1 to 5 ml. Previously heat gently in a reaction vessel a mixture of 3 to 5 ml. of strong phosphoric acid and two or three times as much of the theoretically required amount of potassium iodate until the added potassium iodate disperses into the acid homogeneously. After cooling the contents of vessel, put the weighing tube containing the sample into the vessel along the inside wall of it.

Insert a gas-introducing tube, a thermometer, and a thermometer-protecting tube into the reaction vessel, and connect the reaction vessel with a carbon dioxide generator and a guard tube. Connect a rubber tube R_7 with a suction pump, open the stopcock S_3, and suck up the air present

1) T. Kiba, S. Ohashi, T. Takagi and Y. Hirose, *Japan Analyst*, **2**, 446 (1953).
2) S. Ohashi, This Bulletin, **28**, 171 (1955).

between S_2 and S_3. Now, close the stopcock S_3 and open the stopcock S_2 to fill the container with carbon dioxide. Repeat these operations several times to make sure that no air remains in the container. Finally fill it with carbon dioxide. Next, connect the rubber tube R_7 with an azotometer and open the stopcock S_2, S_3 and S_4 to let carbon dioxide flow through it for two or three minutes. Close the stopcock S_3 and immediately raise the leveling vessel F to fill the azotometer with the potassium hydroxide solution. Then close the stopcock S_4.

Heat the liquid in the reaction vessel A on a small electric heater. During the decomposition reaction shake well the reaction vessel to decompose the sample completely, and keep the temperature of the reactants below 260°C, above which iodic acid is decomposed, liberating oxygen, and leading to a serious error. The end of the decomposition reaction can be easily recognized by the ceasing of the liberation of iodine. Remove the electric heater and transfer the gas in the reaction vessel into the azotometer by carefully opening the stopcock S_2. A part of the iodine liberated is sent into the azotometer and absorbed into the potassium hydroxide solution. Drive the gas in the vessel by letting the carbon dioxide flow, until the gas introduced into the azotometer becomes so-called micro-bubbles.

After standing fifteen minutes, raise the leveling vessel until the solution in it stands at exactly the same height as that in the azotometer. Read the volume of nitrogen, the thermometer, and the barometer.

The percentage of the nitrogen present is computed according to the following equation:

$$\log N\% = \log v + \log g + (1 - \log w).$$

In this equation, $N\%$ represents the percentage of the nitrogen, v the volume (ml.) of the nitrogen measured at t°C and p mm Hg, and g the weight (mg.) of 1 ml. of the nitrogen at t°C and p mm Hg, and w the weight (mg.) of the sample used for the analysis. The value of p mm Hg is obtained by subtracting the aqueous vapor pressure of the 30% potassium hydroxide solution at t°C from the atmospheric pressure measured by means of the barometer.

Results and Discussion

Analyses of various known organic compounds containing nitrogen were made with this method. These results are summarized in Table I.

TABLE I

DETERMINATION OF NITROGEN IN VARIOUS KNOWN ORGANIC COMPOUNDS

Substance	Nitrogen Content %	Sample Weight mg.	Nitrogen Content: Found %	Nitrogen Content: Deviation %
Ammonium chloride NH_4Cl	26.18	15.2	26.6_8	$+0.5_0$
		12.8	26.5_9	$+0.4_1$
		17.8	25.6_3	-0.5_5
		16.6	25.6_2	-0.5_6
		10.8	26.1_8	0.0_0
Ammonium oxalate $(COONH_4)_2 \cdot H_2O$	19.71	25.7	19.4_3	-0.2_5
		21.5	19.4_4	-0.2_7
		24.9	19.0_3	-0.6_2
		10.4	19.5_3	-0.1_8
		15.9	19.5_6	$-.01_5$
Acetanilide $C_6H_5NHCOCH_3$	10.36	34.3	10.3_4	-0.0_2
		27.6	10.1_7	-0.1_9
		19.5	10.4_0	$+0.0_4$
		19.7	10.3_6	0.0_0
		26.5	10.0_3	-0.3_3
Phthalimide $C_6H_4(CO)_2NH$	9.52	18.0	9.23	−0.29
		18.7	9.22	−0.30
Phenacetin $C_2H_5OC_6H_5NHCOCH_3$	7.82	26.1	7.74	−0.08
		44.6	7.76	−0.06
		39.6	7.79	−0.03
		34.4	7.74	−0.08
		32.8	7.91	+0.09
Thionalide $C_{10}H_7NHCOCH_2SH$	6.45	23.2	6.33	−0.12
		11.9	6.28	−0.18
		18.5	6.34	−0.11
		24.1	6.53	+0.08

TABLE I (Contd.)

Substance	Nitrogen Content %	Sample Weight mg.	Nitrogen Content Found %	Nitrogen Content Deviation %
Urea	46.63	9.5	46.0_5	-0.5_8
NH_2CONH_2		9.2	47.2_5	$+0.6_2$
		10.6	46.5_4	-0.0_9
		10.0	46.2_7	-0.3_6
		10.6	45.8_7	-0.7_4
Thiourea	36.81	13.4	36.4_3	-0.3_5
NH_2CSNH_2		23.3	36.2_1	-0.5_5
		10.9	36.2_7	-0.5_4
		14.8	36.8_8	$+0.0_7$
		12.3	36.0_8	-0.7_3
Methyl orange	12.84	16.5	12.7_8	-0.0_5
$(CH_3)_2NC_6H_4NNC_6H_4SO_3Na$		14.0	12.7_2	-0.1_2
		24.7	12.8_5	$+0.0_1$
		14.0	12.9_3	$+0.0_9$
		23.2	12.5_3	-0.2_8
Methyl red	15.61	23.8	15.9_9	$+0.3_8$
$(CH_3)_2NC_6H_4NNC_6H_4COOH$		17.8	15.5_8	-0.0_3
		17.8	15.5_3	-0.0_8
		15.4	15.8_2	$+0.2_1$
		21.0	15.6_5	$+0.0_4$
Dithizone	21.85	23.6	21.2_3	-0.6_2
$C_6H_5NHCSNNC_6H_5$		23.2	21.0_2	-0.8_3
		15.5	21.8_8	$+0.0_3$
		14.0	21.7_8	-0.0_7
		15.0	21.7_7	-0.0_8
DL-Tryptophane	13.72	15.5	13.1_4	-0.5_8
$C_8H_6N \cdot CH_2CH(NH_2)COOH$		23.8	13.5_3	-0.1_8
		10.6	13.3_0	-0.4_2
L-Histidine hydrochloride	20.05	17.4	19.8_7	-0.1_8
$C_3H_3N_2 \cdot CH_2CH(NH_2HCl)COOH \cdot H_2O$		20.7	20.2_7	$+0.2_2$
		27.2	19.7_5	-0.3_0
		20.8	19.5_9	-0.4_7
1-Phenyl-3-methyl-pyrazolone-(5)	16.08	36.50	16.31	+0.23
$CH_3C_3H_2ON_2 \cdot C_6H_5$		32.94	16.35	+0.27
		99.86	15.86	−0.22
		26.93	16.08	0.00
		33.36	16.39	+0.31
2-Aminobenzothiazole	18.65	9.82	18.39	−0.26
$C_7H_4NS \cdot NH_2$		16.76	18.58	−0.07
		22.19	18.24	−0.41
		21.31	18.17	−0.48
Nitron	17.94	19.0	18.1_3	$+0.1_9$
$C_{20}H_{16}N_4$		22.4	18.1_7	$+0.2_3$
		19.0	17.7_9	-0.1_5

Two ammonium salts were also analyzed. As pure samples as possible were selected or prepared and dried in the calcium chloride or sulfuric acid desiccator.

Not only the nitrogen in ammonium salts (ammonium chloride and ammonium oxalate) and amines (acetanilide, phthalimide, phenacetin, thionalide, urea, and thiourea), but also in azo-compounds (methyl orange, methyl red, and dithizone), a pyrrole (DL-tryptophane), pyrazols (L-histidine hydrochloride and 1-phenyl-3-methyl-pyrazolone-(5)), and a thiazole (2-aminobenzothiazole) were determined by means of this method. The nitrogen in the complicated compound such as nitron was also quantitatively determined. The precision and accuracy of the data are within ±3%.

Since it was assumed that the nitrogen in amino acids might be accurately estimated with this method, several amino acids (glycocoll, DL-α-alanine, DL-α-amino-n-valeric acid, L-leucine, DL-isoleucine, L-cystine, and arginine hydrochloride) were analyzed. Analyses for these compounds gave satisfactory results as shown in Table II.

For the compounds containing the already oxidized-form nitrogen such as nitro- or nitroso- radicals this method can not be used.

Uric acid and theobromine, which are derivatives of purine, atropine and lacto-flavine, which have complicated rings containing nitrogen, and antipyrine gave very low results for nitrogen with this method. The reason why this method can be applied to 1-phenyl-3-methyl-pyrazolone-(5), but not to antipirine, although these compounds have similar pyrazol rings, has not yet been determined.

TABLE II

DETERMINATION OF NITROGEN IN SOME AMINO ACIDS

Substance	Nitrogen Content %	Sample Weight mg.	Nitrogen Content Found %	Nitrogen Content Deviation %
Glycocoll NH_2CH_2COOH	18.66	15.3	18.8_5	$+0.1_9$
		24.0	18.1_4	-0.4_2
		21.9	18.3_9	-0.2_7
		19.1	18.8_3	$+0.2_0$
		25.6	18.3_8	-0.2_8
DL-α-Alanine $CH_3CH(NH_2)COOH$	15.76	25.5	15.6_7	-0.1_3
		22.1	15.9_0	$+0.1_4$
		18.1	15.5_3	-0.2_0
		26.2	15.7_6	0.0_0
		25.6	15.3_5	-0.4_0
DL-α-Amino-n-valeric acid $CH_3CH_2CH_2CH(NH_2)COOH$	11.96	30.9	11.6_8	-0.2_8
		20.3	11.8_1	-0.1_5
		18.6	11.5_4	-0.4_2
		35.6	11.7_6	-0.2_0
L-Leucine $(CH_3)_2CHCH_2CH(NH_2)COOH$	10.68	16.3	12.0_4	$+0.0_8$
		21.1	10.6_0	-0.0_8
		18.3	10.5_9	-0.0_9
		21.2	10.9_9	$+0.3_1$
		13.3	10.6_7	-0.0_1
		31.1	10.5_3	-0.1_5
DL-Isoleucine $CH_3CH_2CH(CH_3)CH(NH_2)COOH$	10.68	23.1	10.9_0	$+0.2_2$
		18.3	10.9_7	$+0.2_9$
		19.2	10.6_5	-0.0_3
		15.7	10.2_8	-0.4_0
L-Cystine $(-SCH_2CH(NH_2)COOH)_2$	11.66	20.9	11.3_7	-0.2_9
		20.9	11.4_7	-0.1_9
		28.1	11.6_3	-0.0_3
Arginine hydrochloride $NH_2C(NH)NHCH_2CH_2CH_2$-$CH(NH_2HCl)COOH$	26.60	14.3	26.4_1	-0.1_9
		14.4	26.8_5	$+0.2_5$
		12.3	25.8_9	-0.7_1
		13.7	26.6_9	$+0.0_9$
		18.5	25.8_0	-0.8_0

As has been indicated above this iodic acid decomposition method can be applied to many species of organic compounds containing nitrogen, but not to all species.

The compounds having relatively low melting points such as diphenylamine, p-dimethylaminobenzaldehyde, and azobenzene, the melting points of which are 54, 74, and 68°C, respectively, can not be analyzed with this method, because these compounds are partially volatilized during the decomposition reaction.

It was shown by means of experiments for nicotinic acid and oxine that the nitrogen in pyridine and quinoline ring can not be liberated with this reagent at all. Since the nitrogen in amino-form can be determined with this method as mentioned above, it was presumed that for the two nitrogens of nicotinic amide only the nitrogen in amino-form

TABLE III
DETERMINATION OF NITROGEN IN NICOTINIC AMIDE

Substance	Half the Nitrogen Content %	Sample Weight mg.	Nitrogen Content	
			Found %	Deviation %
Nicotinic amide $C_5H_4N \cdot CONH_2$	11.57	14.8	11.9$_3$	+0.3$_6$
		21.2	11.6$_9$	+0.1$_2$
		19.5	11.6$_8$	+0.1$_1$
		13.8	11.9$_4$	+0.3$_7$

might be measured. As might have been expected half the total nitrogen could be determined as indicated in Table III.

The advantages of this method are as follows: (1) Since the iodic acid decomposition of organic compounds in strong phosphoric acid is a wet reaction, the velocity of the decomposition in this method is much more rapid than in the micro-Dumas method. The time required for one analysis is about thirty to forty minutes. If this method is modified from semi-micro to micro method in the future, the analysis time will be more shortened. (2) The progress of the decomposition reaction can be watched through the glass and the end of its reaction can be easily recognized. Namely, it is indicated by means of the ceasing of the bubble formation and clearing of the liquid. (3) The apparatus is very cheap and all of it can be made by oneself.

The defects of this method are the following: (1) Similarly to the case of the Kjeldahl method, not all types of compounds containing nitrogen can be analyzed with this method as mentioned above. (2) The precision and accuracy of the data in this method are slightly worse than the micro-Dumas or Kjeldahl method. This is probably owing to the imperfection of the apparatus. The improvements of these defects for this method and the modification of this method to the micro scale are the remaining problems for the future.

Summary

A new method has been developed to permit the rapid determination of nitrogen in organic compounds. The sample is decomposed with iodic acid-strong phosphoric acid reagent in a glass reaction vessel, and the liberated nitrogen is collected in an azotometer filled with potassium hydroxide solution by the flow of pure carbon dioxide. From the volume of the nitrogen thus collected the percentage of the nitrogen in the sample can be readily determined. This method is, so to speak, the wet modification of the Dumas method.

For various types of compounds containing nitrogen, ammonium salts, amine, azo-compound, pyrrol, thiazole, etc., satisfactory results were obtained by means of this method. The nitrogen in a 10 to 50 mg. sample can be determined for thirty to forty minutes with a simple and inexpensive apparatus.

But volatile compounds, nitro- or nitroso-compounds, compounds having purine, pyridine, quinoline, and other complicated rings, etc., can not give good results.

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Decrease of the Surface Area of Raney-type Catalysts in the Aluminium-dissolution Process

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Introduction

Some authors have shown[1-5] that the surface areas or the catalytic activities of Raney nickel catalysts decrease on reserving. The present authors suggested in the studies on Raney copper catalyst for the dehydrogenation of cyclohexanol to cyclohexanone,[6] that the similar, but much more rapid decrease of the surface area might occur in the process of dissolving aluminium with alkali.

It has been confirmed that this suggestion was right and applicable also to the usual Raney nickel catalyst.

Experimental Procedure

(1) Preparation of the Catalysts.

a) Starting alloy.—The starting alloy for the catalyst No. 16* was obtained as follows.

Firstly, 40 parts of aluminium were melted in an electrically heated furnace or Tammann furnace and then 5 parts of zinc, 50 parts of copper, and 5 parts of nickel were put into it in the above order.

The fused solution was stirred with a silica tube to be homogenized, the temperature being raised to about 900°C. After cooling the alloy was powdered and 200 mesh powders were used as the sample. The content of aluminium was 40.6%.

As Raney nickel, a commercial one containing 48.9% of aluminium was used.

b) Dissolving of aluminium.—The dissolution of aluminium was carried out using 30% NaOH aqueous solution in an open vessel. After dissolution, the remaining catalyst was taken out of the alkali solution and washed with cold water till the washed water became neutral to litmus-paper. The time required for this treatment was always 3 to 4 hrs.

As soon as the washing was finished the sample was put into a vessel for the measurement of the surface area and dried at 20° to 30°C under the reduced pressure until the pressure of the system reached about 10^{-4} mm Hg.

(2) Measurement of the Surface Area.—The surface area was determined by using the usual method of low temperature adsorption of carbondioxide and making use of the B. E. T. equation. Nitrogen gas was used to the measurement of the dead space of the apparatus.

The carbondioxide that we used was a commercial one stored in an iron cylinder. It was purified by the usual cleaning up system, consisting of a copper sulfate bottle for scrubbing out hydrogen-sulfide, a concentrated sulfuric acid bottle for drying and a phosphorus pentoxide tube for removing the trace of moisture.

After the system was pumped out to high vacuum (about 10^{-4} mm Hg), the first adsorption test of carbon dioxide was carried out at −78.5°C. To avoid errors based on the probable presence of a trace of alkali on the surface of the catalyst, the system was degassed by a diffusion pump for an hour at 0°C after the first test and the adsorption test was repeated again at −78.5°C.

The surface area was calculated from the V_m value (the volume of gas required to form a monomolecular layer all over the surface) obtained from the second isotherm, where the cross-sectional area of carbondioxide molecule was assumed to be 17.0 Å^2.

Results

The experimental results are shown in Fig. 1, Fig. 2, Table I–a and Table I–b.

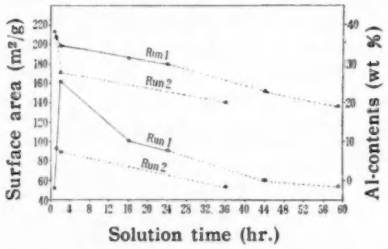

Fig. 1. The relationship between the surface area and the condition of aluminium-dissolution, on the catalyst "No. 16".
⊙ Surface area. ⚠ Content of aluminium. (Temperature of dissolution are 10°to 15°C at solid lines and 70° to 80°C at dotted lines.)

* One of the best catalysts for the dehydrogenation of cyclohexanol to cyclohexanone which was discovered by the present authors.[7]

1) J. Aubry, *Bull. soc. chim.* (France), **5**, 1333 (1938).
2) R. Schröter, *Angew. Chem.*, **54**, 229, 252 (1941).
3) A. A. Pavlic and H. Adkins, *J. Am. Chem. Soc.*, **68**, 1471 (1946).
4) H. A. Smith, W. C. Bedoit and J. F. Fuzek, *J. Am. Chem. Soc.*, **71**, 3769 (1949).
5) J. H. Pattison and F. Degering, *J. Am. Chem. Soc.*, **73**, 486 (1951).
6) This suggestion was presented at the 6th Annual Meeting of the Chemical Society of Japan held at Kyoto, April, 1953.

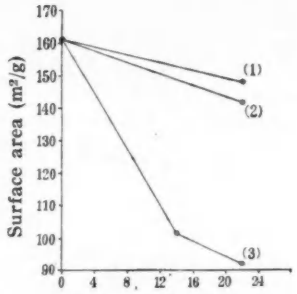

Fig. 2. Variations of the surface area of the catalyst "No. 16" on standing.
Note: Dissolution of aluminium was carried out at 10° to 15°C. for 2 hrs. Each sample was reserved in a following condition.
(1) 70° to 80° C, in vacuum.
(2) room temperature (20°C), in water.
(3) 10° to 15°C, in 30% NaOH aq. solution.

TABLE I-a
VARIATION OF THE SURFACE AREA IN THE ALUMINIUM DISSOLUTION PROCESS ON RANEY NICKEL CATALYST

Condition of the solution		Surface area (m^2/g.)	Al-content (wt%)
1 hr.	10° to 15°C	48.2	33.0
2 hrs.	10° to 15°C	58.8	31.0
24 hrs.	10° to 15°C	47.0	
1 hr. +1 hr.	10° to 15°C 70° to 80°C	43.0	24.8
1 hr.	70° to 80°C	46.5	29.5

TABLE I-b
THERMOSTABILITY OF CATALYST "NO. 16" OBTAINED BY A SEVERE DISSOLUTION PROCESS
(24 hrs., 10° to 15°C+35 hrs., 70° to 80°C)

	Surface area (m^2/g.)	Al-content (wt%)
Original	55.5	19.8
After heating at 400°C for 3 hrs. in vacuum	55.5	19.8

Discussion

From the experimental results above mentioned the following is obvious.

1) At an initial step of the dissolution-process, the content of aluminium becomes lower on the surface of the catalyst and bare copper or nickel atoms, active centers for catalysis, increase in number to form abnormally uneven surfaces having a large area.

At the next step of this process, where the velocity of dissolution of aluminium is rather small and the internal aluminium may be dissolved out, the surface area decreases in spite of successive dissolution of aluminium. It surely leads to a conclusion that during this step nascent bare atoms of nickel or copper formed by dissolution of aluminium move so as to reconfigurate the surface-structure to a more stable one. This kind of reconfiguration (or decrease of surface area) may be sufficiently reasonable, but has not been reported on the Raney type catalyst. As anticipated, the rate of this decrease is higher as the temperature of the dissolution process is higher (Fig. 1 and Table I-a).

2) It is valid to say on the catalyst "No. 16" (Fig. 1 and Fig.2), that the decrease of surface area during the aluminium-dissolution process is more rapid when compared with that during reserving in dried state or in water. Smith,

Fig. 3 The catalyst "No. 16" prepared by an exhaustive dissolution-process (24 hrs. at 10° to 15°C and next 20 hrs., at 70° to 80°C).

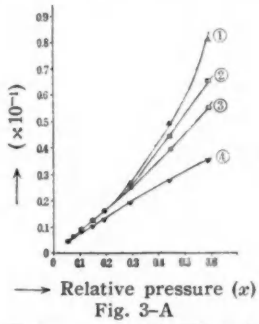

Fig. 3-A
(1) B. E. T.-line. (2) Hüttig-line.
(2) Anderson-line. (4) Langmuir-line.

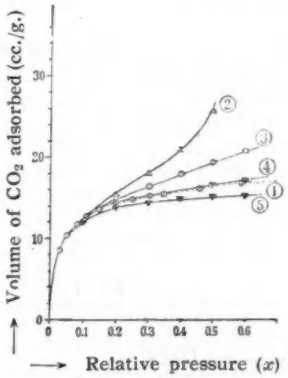

Fig. 3-B
(1) observed-curve. (4) modified B. E. T. -curve (n=2.0).
(2) B. E. T.-curve.
(3) Hüttig-curve. (5) Langmuir-curve.

Bedoit and Fuzek[4] reported the aging of the Raney nickel "W-2", of which the surface area originally was 38.0 m^2/g. and which, after ten or 40 days, decreased to 31.0 or 26.0 m^2/g. respectively. The rate of decrease of surface is merely less than one-tenth compared to that shown in Table I-a.

3) From Table I-b, it can be understood that the catalyst prepared by an exhaustive dissolution-process (24 hrs. at 10° to 15°C, and next 35 hrs. at 70° to 80°C) has a very heat-stable surface. This must be one of the causes that the catalyst maintained the most suitable activity for a long time[8].

4) In Fig. 3-A, the abscissa represents the relative pressure x $(=p/p_0)$, the ordinate $x/v(1-x)$, $x/v(1-0.8x)$, $x(1+x)/x$ or x/v in the case of the B. E. T.[9], Anderson[10], Hüttig[11] or Langmuir[12] equation, respectively (the v is the volume of CO_2 adsorbed).

In each case, the rigid linearity exists at 0.05 to 0.25, 0.05 to 0.25, 0.05 to 0.35 or 0.15 to 0.15 of x, respectively; that is, the Hüttig line shows the linearity in the widest range. (Fig. 3-A)

In Fig. 3-B, solid lines were shown to represent the relations between the relative pressure and the volume of adsorbed carbon-dioxide, calculated by putting each V_m found in Fig. 3-A into the corresponding Hüttig, Langmuir, B. E. T. and modified B. E. T. equation (1)[13] in which the maximum numbers of adsorbed molecules are assumed to be finite.

$$V=\frac{V_m\cdot C\cdot X}{1-x}\cdot\frac{1-(n+1)\cdot x+n\cdot x^{n+1}}{1+(C-1)\cdot x-n\cdot x^{n+1}}, \qquad (1)$$

where C is a constant, and n is the maximum numbers of adsorbed molecules.

A dotted line is the observed curve, which accords best with the modified B. E. T. line $(n=2)$.

5) In Fig. 4-5, calculated values of the adsorbed carbon-dioxide (V_{cal})~the relative pressure lines are shown as dotted lines. The V_{cal} were obtained by putting various finite values in "n" of the modified B. E. T. equation (1), where the V_m found from the B. E. T. line of $x/v(1-x)\sim x$ was always used. Observed curves of the same relation were shown as the solid lines.

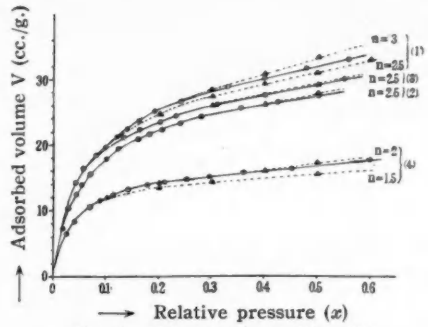

Fig. 4. Alloy-catalyst "No. 16"

Run No.	Condition of aluminium dissolution	n
(1)	16 hrs., 10° to 15°C	2.5-3
(2)	24 hrs., 10° to 15°C	2.5
(3)	1 hr, 10° to 15°C, +1 hr, 70° to 80°C	2.5
(4)	24 hrs, 10° to 15°C+20 hrs, 70° to 80°C	2.0

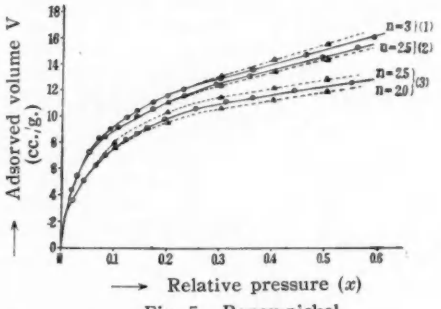

Fig. 5. Raney-nickel

Run No.	Condition of aluminium dissolution	n
(1)	1 hr, 10° to 15°C	3.0
(2)	24 hrs, 10° to 15°C	2.5
(3)	1 hr, 10° to 15°C, +1 hr, 70° to 80°C	$2.0<n<2.5$

A comparison of the curves with the calculated ones shows that the severer the condition of dissolution is, the lower the reliable n-value is. As this value indicates the number of molecular layers adsorbed on the catalyst surface, it may be considered** as a factor indicating the adsorption affinity, which, in turn, probably is a variable having some relation with the catalytic activity.

On dehydrogenation of cyclohexanol to cyclohexanone at 275°C, the catalyst "No. 16" prepared by a mild dissolution process[5] (12°C, 75 hrs.) showed a very high activity in the initial period as compared with the same catalyst prepared by the above exhausive dissolution. But the activity of the former decreased rapidly to a degree lower than that of the latter catalyst, which

7) N. Ohta and M. Sato, *J. Chem. Soc. Japan* (Ind. Chem. Section), **56**, 153, 250 (1953).
8) N. Ohta, M. Sato and J. Imamura, *J. Chem. Soc. Japan*, (Ind. Chem. Section) **56**, 495 (1953).
9) S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).
10) R. B. Anderson, *J. Am. Chem. Soc.*, **68**, 686 (1946).
11) G. F. Hüttig, *Kolloid-Z.*, **121**, 50 (1951).
12) I. Langmuir, *J. Am. Chem. Soc.*, **37**, 1139 (1915), **38**, 2221 (1916).
13) T. L. Hill, *J. Chem. Phys.*, **14**, 263 (1946).

maintained the initial activity for a long time.

It was concluded from these facts that a very active, but unstable surface is left at an initial step of dissolution process in dissolution at a low temperature, while a less active, but more stable surface appears in process of dissolution or the severe dissolution process.

Furthermore, the reconfiguration pointed out at 1) may be an important cause of this decrease of catalytic activity. Active centers on the Raney nickel "W-6"[14], which is the most active catalyst of this type particularly at low temperatures, may seem to be nascent bare nickel atoms formed at the low temperature dissolution.

Summary

Variations of the surface area in the dissolution process were investigated on a Raney copper catalyst "No. 16" (for dehydrogenation of cyclohexanol) and a Raney nickel catalyst.

It has been found that nascent bare atoms of copper or nickel formed at the initial step move rapidly, perhaps particularly in alkali solution, to reconfigurate the surface-structure to a more stable one.

That is to say, the surface area reaches a maximum at an initial step, where only a small quantity of aluminium is dissolved out, then rapidly decreases to a stable value in spite of successive dissolution of aluminium. The rate of decrease is much greater than that recognized on reserving the catalyst in its dried state or in water.

By calculating reliable "n" values, the number of adsorbed molecular layers on the surface area from the modified B. E. T. equation, it has been deduced that the average catalytic activity per unit area of the surface may be decreased in process of dissolution of aluminium.

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Hatagaya

14) H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, 70, 695 (1948).

** The n-value may not be considered as a factor indicating the variation of pore- radius at the catalyst from the adsorption-desorption isotherm.

Surface Chemistry of Synthetic Protein Analogues. VI. The Interaction of Urea and Salt with Non-electrolytic Polypeptides

By Toshizo ISEMURA, Kozo HAMAGUCHI and Hideyo KAWASATO

(Received September 27, 1954)

When protein is spread on the surface of water as a monolayer, it suffers in general surface denaturation. On the other hand, it is also denatured by the interaction with some reagent such as urea. Moreover, it is well known that urea forms adduct compounds[1] with most compounds having a relatively long, straight hydrocarbon chain. The behaviour of the synthetic polypeptides such as poly-DL-α-aminolauric acid etc. which had been investigated as a protein model in the previous experiments,[2] has been studied on the substrate of urea solution by measuring surface pressure-area and surface viscosity-area relations. Meanwhile, the interaction of salt solution on these films of non-electrolytic polypeptides was also investigated. Urea affects the pressure-area relation profoundly, in spite of the absence of -S-S- or -SH groups in these polypeptides, as compared with the protein which contains such groups.

Experimental

The Method and Materials. — The surface pressure was measured by the surface balance of Langmuir-Adam type. The torsion thread used was phosphorbronze wire, 0.12 mm. in diameter. The pressure was measured up to 5 dynes/cm. The surface viscosity was measured by the dumping of the oscillatory rotation of disc. The details of the measurements are essentially the same as those in the previous investigations.[3] The materials were poly-DL-α-aminolauric acid, poly-DL-α-aminocapric acid, poly-DL-α-aminocaprylic acid and poly-γ-benzyl-L-glutamate. The urea used was a commercial product of Toyo Koatsu Kogyo Co., which was used after repeated recrystallization and adsorption by active carbon. Potassium chloride was used as an example of salt in this case. It was a chemical reagent grade and doubly recrystallized.

1) A.E. Smith, *J. Chem. Phys.*, 18, 150 (1950).
2) T. Isemura and K. Hamaguchi, This Bulletin, 25, 40 (1952).
3) T. Isemura and K. Hamaguchi, ibid., 27, 125 (1954).

Experimental Results

The measured surface pressure-area relations are shown in Fig. 1–4. The film expanded considerably on the substrate containing urea. The more urea existed in the substrate, the film the more expanded. The viscosity-area relations on the substrates with or without urea are shown in Fig. 5. The viscosity of the film on the urea containing substrate was rather irregular and the reproducibility of the results was relatively unsatisfactory. The products of pressure and area FA were plotted against pressure F in the low pressure region. Satisfactorily linear relations were obtained as shown in Fig. 6. In each figure, all straight lines intersect FA-axis at a single point.

The effect of potassium chloride is shown in Fig. 7. While potassium chloride affects considerably the F–A curve in the case of electrolytic polypeptide as reported in the preceding paper[4] in the concentration as low

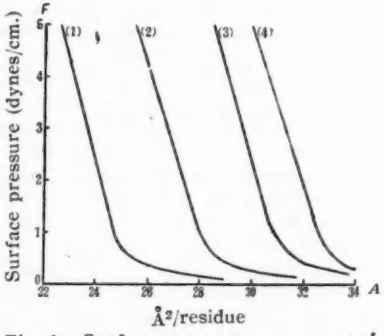


Fig. 1. Surface pressure-area curves of poly DL-α-aminolauric acid. (1) on distilled water; (2) on 10 % urea solution; (3) on 20 % urea solution; (4) on 30 % urea solution.

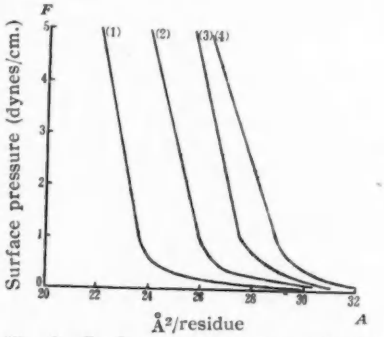


Fig. 2. Surface pressure-area curves of poly DL-α-aminocapric acid. (1) on distilled water; (2) on 10 % urea solution; (3) on 20 % urea solution; (4) on 30 % urea solution.

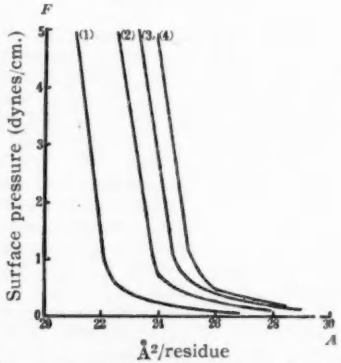


Fig. 3. Surface pressure-area curves of poly DL-α-aminocaprylic acid. (1) on distilled water; (2) on 10 % urea solution; (3) on 20 % urea solution; (4) on 30 % urea solution.

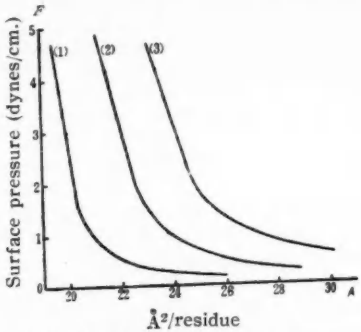


Fig. 4. Surface pressure-area curves of poly γ-benzyl-L-glutamate. (1) on distilled water; (2) on 10 % urea solution; (3) on 30 % urea solution.

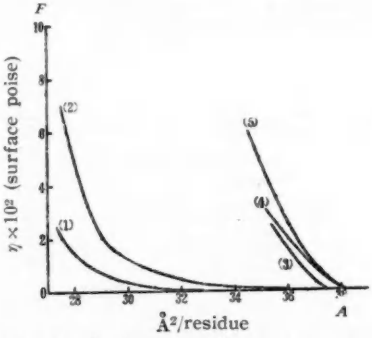


Fig. 5. Surface viscosity-area curves of poly-γ-benzyl-L-glutamate. (1) on distilled water or 0.1 % urea solution; (2) on 0.3 % urea solution; (3) on 0.5 % urea solution; (4) on 5 % urea solution; (5) on 10 % urea solution.

4) K. Hamaguchi and T. Isemura, ibid., 28, 9 (1955).

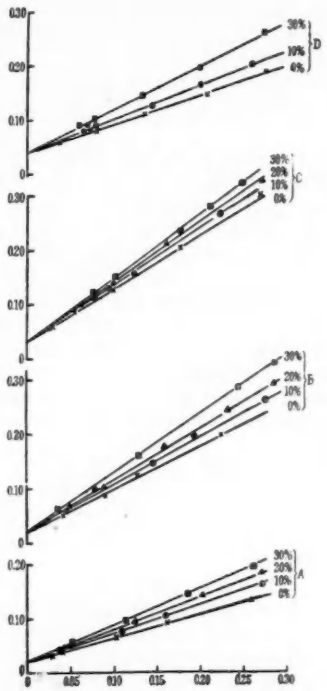


Fig. 6. Plot of FA versus F for poly DL-α-aminolauric acid (A), poly DL-α-aminocapric acid (B), poly DL-α-aminocaprylic acid (C), and poly γ-benzyl-L-glutamate (D).

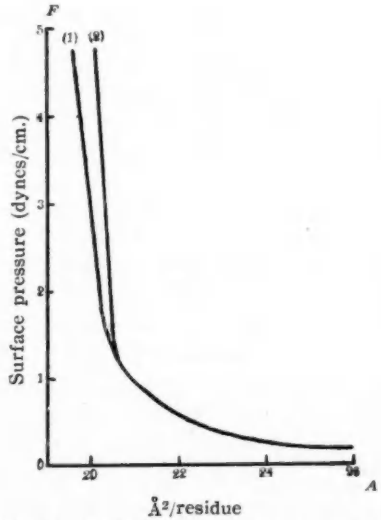


Fig. 7. Surface pressure-area curves of poly γ-benzyl-L-glutamate on distilled water (1) and on 10 % KCL solution (2).

as 0.5 %, it did not affect that of the non-electrolytic polypeptide in the concentration of 1 %. However, the film expanded slightly on 10 % potassium chloride solution.

Discussion

From these experimental results, it might be concluded that the Guastalla's relation[5],

$$FA=\alpha F+\beta$$

holds for the polypeptide films on distilled water as well as on urea solutions. The estimated molecular weights of these polypeptides are shown in Table I.

TABLE I

MOLECULAR WEIGHT DETERMINED ON VARIOUS SUBSTRATES

Substrate sample	Distilled water	10% urea solution	20% urea solution	30% urea solution
Poly-DL-α-amino caprylic acid	74,500	73,500	74,000	74,000
Poly-DL-α-amino capric acid	122,000	111,700	111,700	111,700
Poly-DL-α-amino lauric acid	121,000	122,000	111,500	111,800

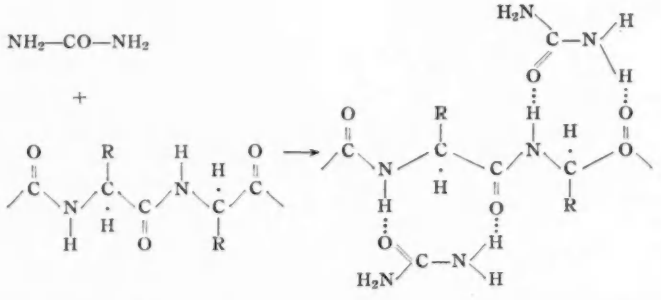
The coincidence of points of intersection made by the FA axis and FA–F lines indicates that the molecule of the polypeptide suffers neither association nor dissociation on the substrate of urea solution. The slopes of these FA–F lines become steeper with the increase of the concentration of urea. As generally accepted, the slopes of these lines correspond to the co-area of the molecule.[5] Therefore, it is very probable that the polypeptide molecule interacts in some way with urea and forms a labile addition compound which occupies a larger area. The interaction was non-stoichiometric because the slope of FA–F lines became steeper when the solution was more concentrated. It does not seem to be caused by the aduct formation, because the expansion of the film was observed on the dilute aqueous urea solution as low as 5 %. This concept is also valid in view of the fact that the film of poly-γ-benzyl-L-glutamate which should not form urea aduct, also expanded on the urea solution, and that the formation of aduct is generally agreed to be difficult with compounds of branched chain or those containing a large group such as benzene in the chain.

If the effect of urea found in the present experiments stands with the urea denaturation of protein, the view that the sulfhydryl groups play a special part in denaturation might be incorrect. Bonding of urea to the

5) J. Guastalla, *Compt. rend.*, 208, 1078 (1938); H.B. Bull, *J. Biol. Chem.*, 185, 27 (1950).

polypeptide linkage replaces the intramolecular hydrogen bondings in protein and leads to the cleavage of salt bridges causing the unfolding of the polypeptide. In our present experiment the polypeptide was unfolded by spreading it as a surface film. Hence, the urea solution as dilute as 5% in concentration will readily interact with polypeptide linkage. The appearance of -SH groups in the protein denatured by the interaction with urea rather means the removal of steric hindrance by neighbouring peptide chains against the reaction with the reagent such as nitroprusside.

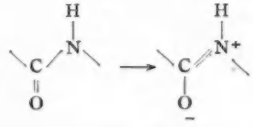
With a given polypeptide sample, all *FA–F* lines obtained with the substrate of different urea content intersect *FA*-axis at a single point as mentioned above. This is a very striking fact, which may be comprehended to be such that the number of polypeptide molecules does not change by the urea interaction. Nevertheless, the co-area of the molecule of film substance increased with the increase of urea concentration in the substrate. It is said that the denaturing action of solution of urea on protein is probably due to the formation of hydrogen bonds with the peptide linkages of the peptide chains[5]. Hence, the expansion of the film might be caused by the bonding of urea to the polypeptide linkage as follows:



Once this bonding was formed, it would be fairly strong. When the substrate water was partially replaced by dropping distilled water of equal volume to that of the through into it at a corner and overflowing the substrate water through syphone from it at its farthest corner without causing any disturbance on the film surface, the film area did not decrease.

A view may be expressed that the expanding effect of urea on the film of polypeptide would be caused by the breaking of the inter- and intrachain hydrogen bonds. However, if that were the case, the number of molecules on substrates of different urea concentrations would have changed and the *FA–A* lines should not intersect *FA* axis at a single point.

It was reported in the previous paper[4] that electrolyte such as potassium chloride exerts a profound influence on the nature of film of amphoteric copolypeptide. However, on the films of non-electrolytic polypeptide as in the present experiment was scarcely detected. On the highly concentrated solution the film non-electrolytic in nature was slightly affected as shown in Fig. 7. The reasons for this expansion of the film might be explained by the formation of rather looser network, by the interaction of polarized backbone as follows.



From the results of the viscosity measurements, the influence of urea was found to be predominant at the concentration more than 0.5% in the substrate. Although the *F–A* curve tends to shift to the larger area on the more concentrated urea solution, the *η–A* curves on the substrates of concentrated urea solution were independent of urea concentration.

Summary

The interaction of urea and potassium chloride with non-electrolytic polypeptide monolayers was investigated. The film of polypeptide was expanded considerably in the presence of urea in the substrate. The number of molecules was, however, not changed by the interaction with urea. The molecular weights of polypeptides determined by surface pressure measurement on the substrates with

6) F. Haurowitz. "Chemistry and Biology of Proteins," Acad. Press, New York, (1950) p. 130.

or without urea were the same. Whereas the co-area of the molecule was increased by increase of urea concentration in the substrate. Urea might be bound to the peptide linkages in backbone by hydrogen bonding and the formation of aduct seems improbable.

Although potassium chloride affected the nature of electrolytic polypeptide film profoundly, it scarcely affected that of the non-electrolytic polypeptide film. The interaction with urea was discussed in relation to the protein denaturation.

The authors wish to express their sincere thanks to Dr. H. Tani and Mr. H. Yuki of the Faculty of Science of Osaka University and Dr. J. Noguchi of Kanazawa University who gave them the valuable samples of the synthetic polypeptides. A part of the expense for this experiment has been defrayed from grants given by the Ministry of Education and by the Asahi Press, to which the authors thanks are also due.

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A Note on Some Alkoxydisilanes

By Rokuro Ōkawara, Toshio Tanaka and Keiichi Maruo

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Many alkoxy-monosilane and -polysiloxanes have been studied, but on the alkoxydisilanes only a few reports[1,2,3] have been presented. The difficulty encountered on preparing the alkoxydisilanes from hexachlorodisilane and alcohol is the fission of Si-Si bond during the reaction. In the fission product, usually, alkoxy-monosilane and -polysiloxanes were found. Among them, disiloxane has a boiling point close to that of disilane and it is difficult to separate these two compounds by distillation. This paper will describe in as great detail as possible the preparation of alkoxydisilanes in the pure state. And the properties of hexamethoxydisilane (I), hexaethoxydisilane (II) and hexaisopropoxydisilane (III) will be described.

As previously reported[3], to prepare (I) from hexachlorodisilane and methanol, the dehydrochlorination by bubbling of nitrogen should be carried out under 30°C to prevent the fission of Si-Si bond also any trace of chlorine compound contaminated in the product should be precipitated by dry ammonia. In the light of this experiment, the preparation method to give pure (II) reported by Martin[1] and followed by Abrahamson et al,[2] appeared questionable. To drive off a trace of chlorine compound from the reaction product, Martin added ethanol and distilled it repeatedly and finally he obtained the chlorine free (II). In our experiment, it was found very difficult to purge off all the chlorine compound by repeated addition of ethanol and by followed aeration even at about 92°−95°C. And the product obtained after distillation still contained a trace of chlorine compound which makes the product slightly turbid and on prolonged standing there was a little precipitation of a white substance.

To assure whether the elevated temperature treatment of dehydrochlorination may give the completely chlorine free product or not the following incompletely dehydrochlorinated mixture of ethanol (6 mol.) and hexachlorodisilane (1 mol.) was refluxed. The chlorine content gradually decreased as in the case of partially alkolyzed alkylchlorosilanes[4,5]. And there was obtained a completely chlorine free product which was assured by Beilstein test. On fractional distillation, tetraethoxysilane, hexaethoxydisiloxane contaminated with a very small amount of (II) and octaethoxytrisiloxane were obtained. From this experiment, it may be concluded that by prolonged heating at the reflux temperature the incompletely dehydrochlorinated ethoxydisilane becomes chlorine free, but the ethoxydisilane is decomposed to form the mixture of the ethoxy-monosilane and -polysiloxanes.

Hexaisopropoxydisilane (III), a crystalline solid having the melting point 84.5° to 84.7°C,

1) G. Martin, *J. Chem. Soc.*, **105**, 2860 (1914).
2) E.W. Abrahamson, I. Joffe and H.W. Post, *J. Org. Chem.*, **13**, 275 (1948).
3) R. Ōkawara and T. Tanaka, This Bulletin, **27**, 120 (1954).
4) R. Ōkawara, This Bulletin, **27**, 428 (1954).
5) R. Ōkawara and I. Ishimaru, ibid., **27**, 582 (1954).

was obtained after repeated recrystallizations from isopropanol. The relation of its melting point and the silicon content was determined after each recrystallization.

Analytical data of silicon of (I) and (II) were somewhat lower than the calculated value, but it may be seen within the experimental error. It may be possible that these two liquid alkoxy-disilanes are contaminated with a small amount of corresponding disiloxane, which has a boiling point close to that of the disilane. To determine the contamination of disiloxane in disilane, the volumetric method of determination of hydrogen evolved on the reaction with a basic reagent may be the suitable one, since with the determination of silicon content it is not easy to differentiate these two compounds. But the volumetric method which was described by Abrahamson[2] and Schumb[6] may not be useful for the time being, for the hydrogen evolved by the fission of Si-Si bond was not quantitative in general.

It was further found that the prevailing method of preparation of alkoxymonosilane using pyridine as an acid acceptor throughout the reaction could not be applied to the preparation of alkoxydisilane, because in pyridine medium, the fission of Si Si bond takes place and alkoxymonosilane becomes the main product.

Experimental

Starting Materials.—For the starting materials dehydrated methanol and ethanol, of which the water content was found by the Karl Fischer method to be 0.05% and 0.17% respectively, and isopropanol of Shell Chemicals (b.p. 82.2°C, n_D^{20} 1.3776) were used. The hexachlorodisilane used in this experiment was prepared by the reaction of chlorine and powdered 75% ferrosilicon at the temperature of 160°–250°C. As the catalyst a small amount of potassium chloride[7] was mixed with the ferrosilicon. The liquid product obtained was rigorously fractionated through a Stedman column of about 30 theoretical plates. The fraction having the boiling point 147°C/760 mmHg and the melting point −1.2°—0.8°C was taken as the starting material. Analysis for the hydrolyzable chlorine was carried out by breaking 0.2–0.5 g. of the weighed sample in water-methanol solution in a sealed vessel, and titrating the liberated acid with 0.1 N-NaOH solution.

Anal. Found: Cl, 79.0. Calcd. for Cl_6Si_2: Cl, 79.1%.

Preparation of Hexamethoxydisilane (I).—The preparation and properties of this compound were already described.[3] Data on this substance are given in Table I.

Preparation of Hexaethoxydisilane (II).—In a 500 cc. three-necked flask equipped with an efficient stirrer, a dropping funnel and a reflux condenser hexachlorodisilane (32 g., 0.119 mol.) was placed. Ethanol (33 g., 0.72 mol.) was added with vigorous stirring for 1 hour. During the addition the temperature was kept below 5°C. After the addition the temperature was raised to 30°C for 30 minutes. The mixture (52 g.) was aerated with dry nitrogen for 2 hours during which the temperature was gradually raised to 50°C. The weight of the mixture lessened to 40 g., where the chlorine content was 9.7%. Aeration was further continued at the room temperature by adding 5 g. of ethanol. After 1.5 hours a product (37 g.) containing 2% chlorine was obtained. A slight excess of pyridine (3 g.) was added to precipitate any trace of chlorine compound. The filtrate (30 g.) was fractionated through a semi-micro Stedman column of about 20 theoretical plates. After a slight excess of pyridine and a small amount of tetraethoxysilane were distilled off, the product was fractionated under 0.8 mmHg. The constant boiling fraction (12 g., 31% of the theory) was obtained, the middle portion of which was analysed. The results are given in Table I.

(i) Preparation of Hexaethoxydisilane (II) by Dehydrochlorination at 95°C.—At the room temperature (10°C), 31 g. (0.115 mol.) of hexachloro-

TABLE I

ALKOXYDISILANES

Formula	Boiling Point °C/mmHg	Melting Point °C	Refractive Index n_D^{20}	Density d_4^{20}	Molecular Weight Found** (Calcd.)	% Si Found (Calcd)
$(CH_3O)_6Si_2$ (I)	100–1/20	—	1.4070	1.095	235 (242)	23.00 (23.18)
$(C_2H_5O)_6Si_2$* (II)	75–6/0.8	—	1.4102	0.9728	318 (327)	17.18 (17.20)
$(i\text{-}C_3H_7O)_6Si_2$ (III)	164–6/38	84.5–7	—	—	415 (411)	13.68 (13.68)

* G. Martin, loc. cit., B. P., 123/15, $n_D^{14.5}$ 1.4134, d_4^{17} 0.9718

** Cryoscopic measurement in benzene

6) W.C. Schumb and R.A. Lefever, *J. Am. Chem. Soc.*, 75, 1513 (1953).

7) D.F. Stedman, U.S.P. 2, 621, 111; *Chem. Abstr.* 47, 3037 (1953).

disilane and 32 g. (0.7 mol.) of ethanol were mixed with vigorous stirring during the course of 40 minutes. The mixture was gradually heated to 60°C for 1.5 hours. At this temperature dehydrochlorination was carried out by bubbling a slow stream of dry nitrogen through the mixture. After 1 hour, the weight of the mixture amounted to 37 g., and the chlorine content was found to be 4.1%. To complete the dehydrochlorination, ethanol (2 g.) was added and nitrogen was bubbled for 3 hours at 70°–80°C. But the product (34 g.) which contains still 2.3% chlorine was obtained. Finally, the product (27 g.) of which chlorine content 0.7% was obtained after repeated addition of 2–3 g. of ethanol (the total amount was 7 g.) and by followed aeration for 8 hours with nitrogen at the temperature of 92°–5°C. After adding a small amount of ethanol, the product was rigorously fractionated through the semi-micro Stedman column under the reduced pressure. The following three fractions were obtained.

Fraction	b.p. (°C/mmHg)	n_D^{20}	%Si (Found)	Weight of the fraction (g.)
A′	79/32	—	—	0.5
B′	75–6/0.8	1.4122	17.28	10
C′	108–10/0.8	1.3963	—	2

The fractions A′, B′ and C′ may be considered tetraethoxysilane (reported[8]: b.p. 77/32, n_D^{20} 1.3837), hexaethoxydisilane (II) and octaethoxytrisiloxane (reported[9]: b.p. 126/0.5, n_D^{20} 1.3948; unpublished author's data: b.p. 107/0.8 mm, n_D^{20} 1.3952). But the fraction B′ was contaminated by a small amount of chlorine compound, which was assured by the Beilstein test. Further the fraction B′ became turbid in moist air and it was difficult to weigh.

(ii) Dehydrochlorination at the Refluxing Temperature.—At the room temperature (10°C), 41 g. (0.15 mol.) of hexachlorodisilane and 42.5 g. (0.9 mol.) of ethanol were mixed with vigorous stirring during the course of 1.5 hours and the mixture was gradually heated to 60°C for 2 hours. Then the mixture (49 g.) of which chlorine content 6.6% was heated to its refluxing temperature in a small flask fitted with a condenser, the upper end of which was connected to a calcium chloride tube. As a volatile chlorine compound was gradually evolved from the mixture, the refluxing temperature rose gradually. After 50 hours of refluxing, the temperature attained to 187°C and the chlorine was not found in the mixture by the Beilstein test. The product (41 g.) was rigorously fractionated through the semi-micro Stedman column. The following three fractions were obtained.

Fraction	b.p. (°C/mmHg)	n_D^{20}	%Si (Found)	Volume of the fraction (cc.)
A	57/10	1.3822	—	14
B	76–7/1	1.3928	16.26	4
C	105/1	1.3956	17.46	3

The fractions A, B and C may be considered tetraethoxysilane, hexaethoxydisiloxane (Anal. Calcd. Si, 16.40%. reported[9]: b.p. 94/0.5, n_D^{20} 1.3914) and octaethoxytrisiloxane (Anal. Calcd. Si, 17.68%).

From the silicon content, hexaethoxydisilane (II) which may appear in the fraction B was not found in this experiment. A qualitative test of Si-Si bond in the fraction B and in the residue by the saturated potassium hydroxide solution, showed that the fraction B evolved a very small volume of hydrogen, while the residue evolved hydrogen violently, showing the presence of the compound having Si-Si bond.

From the result of the elevated temperature treatment described here, it was clearly shown that the preparation of alkoxydisilane should be carried out at as low a temperature as possible.

Hexaisopropoxydisilane (III).—In a 300 cc. three necked flask equipped with an efficient stirrer, a dropping funnel and a reflux condenser, hexachlorodisilane (40 g., 0.15 mol.) was placed. Isopropanol (54 g., 0.9 mol.) was added with vigorous stirring for 70 minutes. During the addition the temperature was kept below 5°C. After addition the temperature was gradually raised to 80°C for 2 hours and at this temperature, the mixture was dehydrochlorinated by bubbling dry nitrogen through the mixture until the chlorine content of the mixture became constant (the final value, 2.7%, was attained after bubbling for 4 hours). At this stage the weight of the mixture amounted to 47 g. When the mixture was cooled to the room temperature (10°C), there was a deposit of crystalline matters. The crystals were filtered and recrystallized from ethyl ether, but the crystals could not be completely separated from the fuming matter which may be chloroisopropoxydisilane. To prepare the pure hexaisopropoxydisilane, 3.5 g. of pyridine and 3 g. of isopropanol were added to the mixture (47 g.) and the mixture was maintained at 60°C for 2 hours. The deposited pyridine hydrochloride was filtered off at the temperature of 85°C. The pure hexaisopropoxydisilane could be prepared from recrystallization (a) or distillation (b) of this mixture (40 g.).

(a) Recrystallization.—The crystal was recrystallized four times from isopropanol, and its melting point and silicon content were determined. The results were as follows:

Sample			Recrystallization times 1	2	3	4
(a)	Filtered at 85°C	m.p. (°C)	73–4	81–3	84.5–4.7	84.5–4.7
		% Si	14.4	13.70	13.69	13.74
(b)	(a) was simply distilled	m.p. (°C)	84.5–4.7	84.5–4.7	—	—
		% Si	13.63	13.65	—	—

8) D. F. Peppard, W.G. Brown and W.C. Johnson, *J. Am. Chem. Soc.*, **68**, 77 (1946).
9) T. Takatani, *J. Chem. Soc. Japan (Pure Chem. Section)*, **73**, 409 (1952), (in Japanese).

(b) Distillation.—The mixture (40 g.) was distilled under reduced pressure. The first fraction distilled at the temperature 90°–164°C/38 mmHg (5 g.) and the second constant boiling fraction 164°–6°C/38 mmHg (22 g., 36% theory) of hexaisopropoxydisilane (III) was obtained. The residue was composed of a gelatinous mass and amounted to 12 g. By the analyses of silicon (13.9%) and its melting point (72.5°–76°C), the second fraction may be considered as the crude (III). Pure hexaisopropoxydisilane (III) was obtained by the recrystallization from isopropanol. The properties of this substance are given in Table I. The relation between the melting point and the silicon content after each recrystallization is already shown above together with (a).

Reaction of Hexachlorodisilane and Alcohol in Pyridine-Benzene Solution (i) *In isopropanol.*—In the 500 cc. three-necked flask cooled with ice-bath and equipped as above, 38 g. (0.14 mol.) of hexachlorodisilane diluted with 125 g. of benzene was placed. To this mixture 51 g. (0.85 mol.) of isopropanol mixed with 67 g. (0.84 mol.) of pyridine was added with vigorous stirring. After pyridine hydrochloride was filtered off and benzene was distilled, the product with slight excess of pyridine amounted to 49 g. The product was distilled under reduced pressure. The distillate boiling at the temperature of 70°–110°C/13 mmHg (33 g.) was washed with water and dehydrated with sodium sulphate. From the refractive index n_D^{20} 1.3850, and density d_4^{20} 0.8770 (reported:[10] b.p. 93.4°C/28 mmHg, n_D^{20} 1.3835 and d_4^{20} 0.8744), the distillate was found to be tetraisopropoxysilane, which was produced by the fission of Si-Si bond. The oily residue 17 g. was not further examined.

(ii) *In ethanol.*—To the mixture of hexachlorodisilane (30 g., 0.11 mol.) and benzene was added the mixture of ethanol (32 g., 0.7 mol.) and pyridine (55 g., 0.7 mol.) and treated in the same way as above. After simple distillation the fraction boiling at 55°–65°C/10 mmHg and the residue (10 g.) were obtained. The slightly turbid distillate was thoroughly washed with water and dehydrated on sodium sulfate. From its density (d_4^{20} 0.9330), the distillate may be considered to be tetraethoxysilane (reported[11] : d_4^{20} 0.9356).

10) R. Okawara, T. Tanaka and I. Ishimaru, This Bulletin, **27**, 45 (1954).
11) H. D. Cogan and C. A. Setterstrom, *Ind. Eng. Chem.*, **39**, 1364 (1947).

Analyses

Silicon.—Silicon was determined by decomposing the sample with concentrated sulfuric acid.

Hydrogen.—Only qualitative tests were carried out with the three disilanes by using the Zerewitinoff apparatus. Hexamethoxydisilane (I) evolved about 94% theory of hydrogen by mixing butanol saturated with sodium hydroxide at the room temperature (8°C), while hexaethoxydisilane (II) on the same condition became a gel and scarcely evolved hydrogen. By adding a saturated aqueous solution of potassium hydroxide, hexaethoxydisilane (II) easily evolved hydrogen (ca. 94% of the theory), but by 30% aqueous solution, it was difficult to evolve hydrogen. Since isopropoxydisilane (III) floats on the surface of saturated aqueous solution of potassium hydroxide, it was dissolved in dry piperidine and mixed with wet piperidine. Hydrogen evolved very slowly and the volume of it reached to ca. 90% of the theory after standing over night.

Summary

1) Hexamethoxy-, hexaethoxy- and hexaisopropoxy-disilane were prepared and characterized.

2) Dehydrochlorination at an elevated temperature was not suitable for the preparation.

3) A trace of chlorine compound contaminated in the product could be completely taken off by dry ammonia or pyridine.

4) Alkoxydisilanes could not be prepared by using pyridine throughout the reaction as an acid acceptor.

5) The volume of hydrogen evolved by the fission of alkoxydisilanes varied with the reagents.

The authors wish to express their sincere thanks to Dr. Watase for his gracious encouragement and Miss Ukiko Takahashi for her aid during this experiment. Our thanks are also due to the Ministry of Education for aid in this research.

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The Dielectric Constant of 1,4-Dioxane

By Masasi YASUMI and Michio SHIRAI

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The possibility of a significant contribution of the atomic polarization to the dielectric constant of the polyatomic molecule was discussed by Van Vleck.[1] The experimental evidences were obtained by Sutton et al.[2], for the substances considered as nonpolar stereochemically. Their conclusions were based upon the following facts:

1) The molecular polarization of the gaseous substance was independent of the temperature over a wide range.

2) The value of the molecular polarization for the gaseous substances agreed with that obtained by the solution method.

3) The molecular polarization obtained by the solution method was independent of the solvent used.

In the present work we shall propose new criteria for determining whether the molecular polarization is due to the atomic polarization plus electronic polarization.

A) If the value of the molecular polarization in the pure liquid state does not depend upon the temperature.

B) If the molecular polarization in the solution states is dependent neither on concentration nor on the species of solvent.

C) If the molecular polarization in the solid state does not depend upon the temperature.

D) If the obtained values in the various states are consistent with each other.

Then we may conclude that the molecular polarization is simply the sum of the atomic polarization and electronic polarization except in very special cases.*

We shall apply these criteria to the 1,4-dioxane, and shall conclude that we cannot exclude the explanation that the dioxane molecule has only nonpolar form and the observed molecular polarization consists of the atomic and of the electronic polarizations.

The dielectric constant of dioxane in the gaseous state was measured by M. Kubo.[3] The molecular polarization was calculated in the usual way. The obtained value is about 5 cc. greater than the electronic polarization. It was concluded that the difference between the molecular polarization and the electronic polarization is due partly to the orientation polarization of the dioxane molecules in the polar form (or "boat" form) which exist in a small amount in the nonpolar form (or "chair" form). An alternative possibility that the difference is due entirely to atomic polarization of the molecule in the nonpolar form, was considered by the author to be less likely, for he believed that the atomic polarization is equal to about 10% of the electronic polarization.

The statement that the atomic polarization is approximately equal to 10% of the electronic polarization was not proved theoretically[1] but was merely guessed from analogy to the case of compounds,[4] which, however, have only one bond of an appreciable moment or have a rigid structure. If the vibrations of a molecule are harmonic and are not influenced by a neighbouring molecule, then the atomic polarization is independent of the temperature and of the states (gas, liquid, solution, solid). On the other hand, if we find that the molecular polarization of a substance depends neither upon the temperature over a wide range nor upon the state, we can conclude that the molecule of the concerned substance is nonpolar and the molecular polarization is due to the atomic and electronic polarizations. (It may happen that exceptions exist.)

To determine whether the molecular polarization of the dioxane is due to the atomic and electronic polarization, we have measured the dielectric constant of the substance in the liquid state and the solid state. Also the dielectric constants of the dioxane solutions of various concentrations in various solvents (hexane, heptane, cyclohexane and benzene) are measured.

The measurement of the dielectric constant in the solid state is very important to determine if the substance is polar or nonpolar. The dielectric constants of most of the polar substances suddenly decrease to lower values

1) J.H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities", (1932) p. 51, 68. Oxford, Clarendon Press.

2) I.E. Coop and L.E. Sutton, *J. Chem. Soc.*, 1938, 1269.

* It must be noted that the inverse statement is not always valid. It may happen that the atomic polarization is dependent upon the temperature and upon the states.

3) M. Kubo, *Sci. Pap. Inst. Phys. Chem. Res.* (*Tokyo*), 30, 238 (1936).

4) M. Kubo, *Sci. Pap. Inst. Phys. Chem. Res.*, 29, 122 (1936).

when they go from the liquid state to the solid state. Some substances behave similarly at the transition point in the solid state[5]. Consequently, if we measure the dielectric constant of the substance concerned in the solid state from melting point to a much lower temperature, we can determine if the substance is polar or nonpolar.

Our plan is to measure the dielectric constant of dioxane in the liquid state and in the solid state, and to measure those of solutions, to calculate the molecular polarization using Clausius-Mosotti relation, and to see whether it is constant or not.

Experimental

The dielectric constant was measured by a resonance method. (Fig. 1.) The replaceable capacity (liquid cell, C also used for solid) was incorporated into the circuit of a Hartley oscillator (A), the signal from which was picked up in an adjacent wave-meter (B). Each electrical component was enclosed in an earthened metal box.

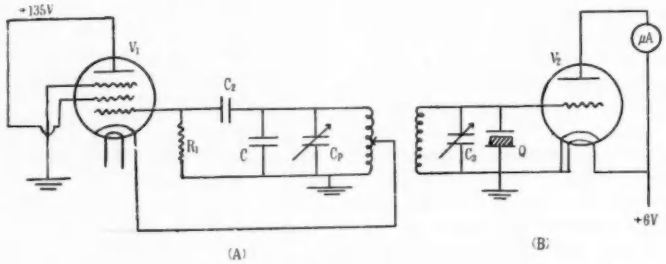

Fig. 1.

V_1: UZ-6C6
V_2: UY-76
C_p: Precision variable air condenser
C_2: Fixed condenser 60 pF
C_3: Air condenser 300 pF
Q : 2 Mc. Resonance quartz
R_1: Fixed resistance 30 kΩ
C : Liquid Cell

The resonance frequency of the wave-meter (B), when the quartz piece Q was not in the circuit, was arranged so that it would at the natural frequency of the quartz piece Q. When the frequency of the oscillator (A) was nearly the same as that of the wave-meter the anode current in the wave-meter humped, and when exactly the same it fell down. The resonance point thus indicated was very sharp.[6]

Precision Condenser C_p.—This was made by Yokogawa Electric Co. Ltd. The working range is 500 pF traversed in 25 turns. Each division (1/100 turn) corresponds to 0.2 pF. The limit of the reading is 1/10 of this division.

Liquid Cell C.—This was made up of two concentric nickel cylinders sealed into a glass vessel. This cell is similar to that used by Mizushima et al.[7] The cell constant did not change when the liquid froze. The capacity of the cell was about 24 pF.

The cell was immersed in a constant temperature bath filled with toluene, and was fixed at a definite position. Low temperatures were obtained by adding dry ice pieces to the bath. The low temperature was measured with an ether thermometer.

The densities of the liquid near room temperature were measured with an Ostwald's pycnometer. The densities of solid were measured with a dilatometer made of a glass tube having a capacity of ca. 5 cc.

The cell constant was determined using benzene as the standard whose dielectric constant was assumed to be 2.2423 at 20°C.

In order to determine the dielectric constant of a solid, it must be considered whether the thermal equilibrium was attained or not. In our experiment, however, it seems that the thermal equilibrium was attained. The reason is as follows: We have measured the dielectric constant of the solid after half an hour from the time when the temperature became constant. After two hours the dielectric constant was re-measured. (The constancy of the temperature was maintained in this time interval). The obtained values are consistent within experimental errors.

Materials used were as follows.

Dioxane.—Commercial dioxane was treated with potassium hydroxide. After distillation over potassium hydroxide, it was fractionally distilled over metallic sodium, a fraction of b. p. 101.5° C being taken.

5) S.O. Morgan, *Ann. New York Acad. Sci.*, XL, 357 (1940).

6) As to the detailed description of the apparatus and procedure of the measurement; see R.J.W. Le Fèvre, "Dipole moment", Methuen's monograph on physical subjects; Methuen Co. Ltd., London (1953), p. 36.

7) S. Mizushima, Y. Morino and K. Higasi, *Sci. Pap. Inst. Phys. Chem. Res.* (*Tokyo*), **25**, 159 (1934).

Benzene.—Commercial benzene was washed with concentrated sulfuric acid, then with water, and was dried over calcium chloride. After drying over metallic sodium, it was fractionally distilled, b. p. 80°C.

***n*-Heptane.**—Commercial *n*-heptane was washed with sulfuric acid, then with water. After drying over calcium chloride, it was distilled, b. p. 97.5°C.

Cyclohexane.—Commercial cyclohexane was dried over calcium chloride, it was then distilled. After drying over metallic sodium, it was fractionally distilled, the fraction of b. p. 81°C being taken.

Experimental Results and Discussions

In Table I are given the values of dielectric constants ε, densities d and molecular polarizations (P_M)* for dioxane in the liquid and the solid state for various temperatures. The values of $P_M - P_E$ are also given in Table I. P_E denotes the electronic polarization, the value of molecular refraction extrapolated to infinite wave-length and amounts to 20.8 cc.

TABLE I

DIELECTRIC CONSTANT OF DIOXANE IN THE LIQUID AND THE SOLID STATE

t	ε	d	P_M(cc.)	$P_M - P_E$(cc.)
60	2.185	0.9911	25.2	4.4
50	2.194	1.0023	25.1	4.3
40	2.206	1.0126	25.0	4.2
30	2.220	1.0220	24.9	4.1
20	2.233	1.0321	24.9	4.1
15	2.248	1.0386	25.0	4.2
12	2.251	1.0416	24.9	4.1
m.p. 11.7				
11	2.329	1.0880	24.9	4.1
10	2.339			
0	2.329			
−10	2.331			
−20	2.331			
−30	2.329			
−40	2.329			
−50	2.329			
−60	2.329			
−70	2.329			

The values of dielectric constanst ε and of densities d for dioxane-hexane solutions at the temperature of 20° C for various molecular fractions x are tabulated in Table II. The molecular polarizations of dioxane are calculated in the usual way,[8] and are tabulated also in Table II, the values of $P_M - P_E$ are shown in Table II.

TABLE II

DIELECTRIC CONSTANT OF DIOXANE-*n*-HEPTANE SOLUTION AT 20°C

x	ε	d	P_M(cc.)	$P_M - P_E$(cc.)
0.0000	1.9491	0.6870	—	—
0.2085	1.9780	0.7287	25.0	4.2
0.4359	2.0251	0.7884	25.0	4.2
0.6282	0.0786	0.8533	24.9	4.1
0.7488	2.1235	0.9026	24.9	4.1
1.0000	2.2326	1.0321	24.9	4.1

In Tables III and IV are given the abovementioned values for dioxane-benzene and dioxane-cyclohexane solutions at the temperature of 20° C and 40° C respectively.

TABLE III

DIELECTRIC CONSTANT OF DIOXANE-BENZENE SOLUTION

t=20° C

x	ε	d	P_M	$P_M - P_E$
0.0000	2.2825	0.8770	—	—
0.1874	2.2751	0.9068	24.7	3.9
0.3498	2.2751	0.9315	24.7	3.9
0.5630	2.2635	0.9640	25.0	4.2
0.7128	2.2529	0.9880	24.9	4.1

t=40° C

x	ε	d	P_M	$P_M - P_E$
0.0000	2.2423	0.8583	—	—
0.1874	2.2423	0.8862	25.4	4.6
0.3498	2.2423	0.9106	25.4	4.6
0.5630	2.2266	0.9428	25.1	4.2
0.7128	2.2193	0.9663	25.0	4.2

TABLE IV

DIELECTRIC CONSTANT OF DIOXANE-CYCLOHEXANE SOLUTION

t=20° C

x	ε	d	P_M	$P_M - P_E$
0.0000	2.0483	0.7789	—	—
0.1715	2.0740	0.8093	25.9	5.1
0.3525	2.1066	0.8471	25.8	5.0
0.5476	2.1437	0.8951	25.5	4.7
0.7156	2.1872	0.9408	25.5	4.7

t=40° C

x	ε	d	P_M	$P_M - P_E$
0.0000	2.0059	0.7616	—	—
0.1715	2.0271	0.7902	25.6	4.8
0.3525	2 0579	0.8278	25.4	4.6
0.5476	2.0971	0.8749	25.3	4.5
0.7156	2.1310	0.9197	25.2	4.4

We see from Table I, that the value of molecular polarization of dioxane is constant over a wide temperature range, on solidification the value of molecular polarization does not change and maintains the same value down to −70° C. The fluctuation of the value is only about 1%, (mean value: 24.9 cc.).

From Tables II and IV, it is shown that the molecular polarization of dioxane in the

* $P_M = \frac{\varepsilon-1}{\varepsilon+2}\frac{M}{d}$; where M is molecular weight of dioxane.

8) P. Debye, "Polare Molekeln", (1929), p. 46, Leipzig.

various solutions are consistent with each other and with that for pure dioxane in the liquid and the solid state. The deviations from the mean value (25.2 cc.) are slightly greater than that for pure dioxane but does not exceed 4%.

The values obtained by M. Kubo for dioxane in the gaseous state are tabulated in Table V.

TABLE V
DIELECTRIC POLARIZATION OF DIOXANE IN THE GASEOUS STATE

T(K)	P(cc.)
328.7	26.39
352.1	26.20
412.4	25.91
478.9	25.95

The difference between the values for the gaseous state and those for the solid and the liquid state is about 1 cc.

The structure of the 1,4-dioxane molecule has been investigated by various methods. X-ray data for the structure of the molecule seem to be lacking. The electron diffraction data[9,10] showed that the molecule exists predominantly in the nonpolar "chair" form[11,12].

The dielectric constants of dioxane in the gaseous state have been measured by M. Kubo[3]. It was concluded that the molecules of dioxane exists predominantly in the "chair" form, but a small amount of the molecule exists in the polar "boat" form. This conclusion was based upon the assumption that the atomic polarization is equal to 10% of the electronic polarization.

The value of the atomic polarization of N one-dimensional oscilator is calculated[1] by the following equation, provided that the latter is harmonic.

$$_AP_i = \frac{Ne_i^2}{4\pi m_i \nu_i^2} = \frac{4\pi N e_i^2}{9 f_i} \qquad (1)$$

where m_i denotes the effective mass, e_i effective charge, ν_i frequency and f_i force constant, respectively.

For the bending vibration (replacing e_i/f_i by μ_i^2/V_i) equation (1) is reduced to

$$_AP_i = \frac{4\pi \mu_i^2}{9 V_i} \qquad (1')$$

where μ_i is bond moment and V_i is force constant for bending.

From equation (1) or (1') we see that the smaller the frequency (or the smaller the force constant) the greater the atomic polarization. In a complex polyatomic molecule, such as 1,4 dioxane, there exist many normal vibrations, some of which may have small frequencies. If they are infra-active, their contribution to the atomic polarization may be considerably significant.

The vibrational frequencies of the dioxane molecule have been observed[9,10], except for the infra-active vibrations of small frequencies. However, the calculation of the frequencies of skeletal vibrations has been made for the "chair" form of the molecule, and it is shown that the frequencies of infra-red active deformation vibrations are about 200 cm^{-1}.

It may be expected, that the atomic polarization of the dioxane molecule in the "chair" form exceeds 10% of the electronic polarization.

So there is no evidence that we cannot attribute the observed difference between the molecular polarization and the electronic polarization entirely to the atomic polarization of the dioxane molecule in the nonpolar "chair" form.

In the following paper the theoretical calculation of the value of the atomic polarization for the dioxane molecule in the nonpolar "chair" form will be given.

We are grateful to Prof. San-ichiro Mizushima for his kind advice and encouragement throughout this work. Our thanks are also due to the Ministry of Education for a grant in aid of this research.

Summary

The dielectric constant of pure dioxane was measured in the liquid and the solid state.

The dielectric constants of dioxane solutions dissolved in various solvents were also measured.

Using Clausius-Mosotti relation, the molecular polarization of dioxane was computed. The computed value was dependent neither upon the state (solid liquid, solution) nor upon the temperature, and agreed almost exactly with the value obtained from the measurement for the gaseous substance.

The difference between the molecular polarization and the electronic polarization is ca. 4 cc. It seems natural to attribute this value to atomic polarization.

Institute of Science and Technology, University of Tokyo

9) L.E. Sutton and L.O. Brockway, *J. Am. Chem. Soc.*, **57**, 473 (1935).
10) O. Hassel, *Fra. Fysik. Verden*, **7**, 1648 (1947).
11) D. A. Ramsay, *Proc. Roy. Soc. S. A.* **190**, 562 (1947).
12) S.C. Burket and R.M. Badger, *J. Am. Chem. Soc.*, **72**, 4397 (1950).

Antituberculous Compounds. V. 1-Thiocarbamyl-3-methyl-5-phenyl-2-pyrazoline, 1-thiocarbamyl-3-methyl-5-(4-nitrophenyl)-2-pyrazoline, and Related Compounds

By Tamio NISHIMURA

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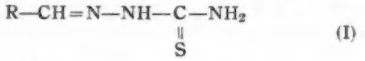
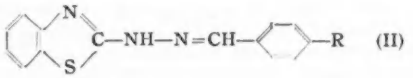
Considerable interest has been aroused by the publication of Domagk, Behnisch, Mietzsch, and Schmidt concerning the antituberculous activity *in vitro* of several thiosemicarbazones of aromatic aldehydes and ketones.[1] An excellent review of the investigation developed by the German workers in correlating structure with activity appeared in 1950.[2] Hoggarth, Martin, Storey, and Young[3] published in 1949 their excellent quantitative *in vivo* evaluation of a considerable number of thiosemicarbazones and compounds of related structure. Furthermore, the extensive synthesis[4] of thiosemicarbazones and related substances, and their *in vitro*[5] and *in vivo*[6] activities were reported by Bernstein et al.

L. Katz[7] prepared a series of the condensation products (II) closely related to the thiosemicarbazone (I), of 2-hydrazinobenzothiazoles with aromatic aldehydes and reported that most active compounds were obtained when the *p*-substituents (R) were carboxymethoxy and dimethylamino radicals.

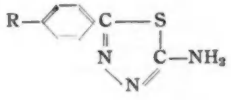


(I)

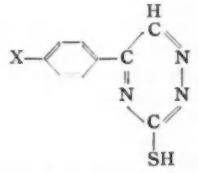


(II)

Bernstein et al.[4] mentioned the preparation of a number of heterocyclic compounds structurally related to I; 5-substituted-2-amino-1,3,4-thiadiazole derivatives (III), and N-(2-benzothiazolyl)-N′-(4-substituted benzal) hydrazone (II). R. Fusco et al.[8,8a] described the synthesis of 5-aryl-3-mercapto-1,2,4-triazines (IV) as new synthetic antitubercular agents.

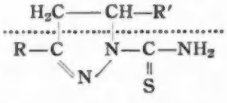


(III)



(IV)

However, the evaluation of 1-thiocarbamyl-2-pyrazolines (V) against *Mycobacterium tuberculosis* has not been reported. A study was therefore inaugurated in this Laboratory with the aim of preparing a number of 1-thiocarbamyl-2-pyrazolines and related substances. It is clear that the structure below the dotted line of (V) coincides with that of the thiosemicarbazone (I). Such a similarity between (V) and (I) was the basis for expecting antitubercular activity in this class of compounds.



(V)

The compounds prepared were 3-methyl-5-phenyl-2-pyrazoline, 3-methyl-5-(4-nitrophenyl)-2-pyrazoline, and their 1-substituted derivatives. The 1-substituents included the $-CS-NH_2$, $-CS-NHC_6H_5$, $-CS-NHCOC_6H_5$, $-CHO$, $-COCH_3$, and $-C_6H_5$ groups. The compounds described herein were prepared as indicated in the flow sheet.

1) G. Domagk, R. Behnish, F. Mietzch and H. Schmidt, *Naturw.*, **33**, 315 (1946); *Chem. Abstr.*, **43**, 3523e (1949).

2) R. Behnisch, F. Miezsch and H. Schmidt, *Am. Rev. Tuberc.*, **61**, 1 (1950).

3) E. Hoggart, A.E. Martin, N.E. Storey, and E.H.P. Young, *Brit. J. Pharm.*, **4**, 248 (1949).

4) J. Bernstein, H.L. Yale, K. Losee, M. Holsing, J. Martins, and W.A. Lott, *J. Am. Chem. Soc.*, **73**, 906 (1951).

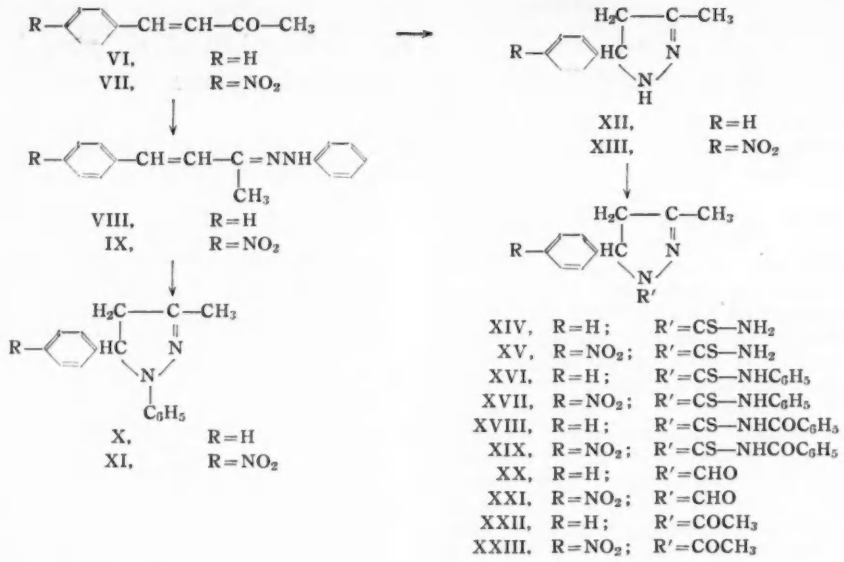
5) R. Donovick, F. Pansy, G. Stryker and J. Bernstein, *J. Bacteriol.*, **59**, 667 (1950).

6) D. Hamre, J. Bernstein and R. Donovick, ibid. 675.

7) Leon Katz, *J. Am. Chem. Soc.* **73**, 4007 (1951).

8) R. Fusco, P. Mantegazza, S. Rossi and R. Tommasini, *Boll. soc. ital. biol. sper.*, **27**, 1730-2 (1951); *Chemi. Abstr.*, **46**, 9199 (1952).

8a) R. Fusco, S. Rossi, G. Mantegazza and R. Tommasini, *Ann. chim.* (Rome), **42**, 94-104 (1952); *Chem. Abstr.*, **47**, 4301*c* 1953).



Benzalacetone (VI) was prepared according to the method described in Organic Syntheses,[9] and *p*-nitrobenzalacetone (VII) according to the procedure reported previously.[10] (VI) and (VII) were converted to the phenylhydrazones (VIII, IX) which were then cyclized to the pyrazolines (X, XI) by heating with glacial acetic acid. 3-Methyl-5-phenyl-2-pyrazoline (XII) was obtained in a 67% yield by the action of 80% hydrazine hydrate upon (VI) in ethanol according to the description of Beech et al.[11] (VII) and hydrazine hydrate in ethanol gave smoothly 3-methyl-5-(4-nitrophenyl)-2-pyrazoline (XIII) at room temperature. 1-Thiocarbamyl-3-methyl-5-(4-nitrophenyl)-2-pyrazoline (XV) was obtained in small yields when (XIII) and pottasium thiocyanate in water was acidified with glacial acetic acid and then heated on a water bath, a considerable amount of the 1-acetyl derivative being isolated from the reaction mixture, whereas in good yields when acidified with hydrochloric acid. On the basis of this finding, 1-thiocarbamyl-3-methyl-5-phenyl-2-pyrazoline (XIV) was easily obtained by the same procedure. The 1-(N-phenylthiocarbamyl)-derivatives (XVI, XVII) were prepared by the action of phenylisothiocyanate on (XII) and (XIII) in petroleum ether at room temperature. The 1-(N-benzoylthiocarbamyl)-derivatives (XVIII, XIX) were obtained by the action of ammonium thiocyanate plus benzoyl chloride on (XII) and (XIII). (XII) and (XIII) were easily converted to 1-formyl derivatives (XX, XXI) by heating with formic acid and to 1-acetyl derivatives (XXII, XXIII) by heating with glacial acetic acid.

9) N.L. Drake and P. Allen, Jr., "Organic Syntheses" Coll. Vol. I, p. 77 (1946).
10) Tamio Nishimura, This Bulletin, **26**, 253 (1953).
11) S.G. Beech, J.H. Turnbull and Walter Wilson, *J. Chem. Soc.* **1952**, 4689.

Experimental

Benzalacetone phenylhydrazone (VIII).—Heating a mixture of benzalacetone (1.4 g.), phenylhydrazine hydrochloride (1.5 g.), sodium acetate trihydrate (1.6 g.), and methanol (20 cc.) gave 1.8 g. (76%) of the desired product melting at 152–158°. Recrystallization from methanol yielded yellow plates melting at 155–157°.[12]

4-Nitrobenzalacetone phenylhydrazone (IX).—By the foregoing procedure, an almost quantitative yield of the hydrazone was obtained in red microcrystals melting at 194–196°.[14]

1-Phenyl-3-methyl-5-phenyl-2-pyrazoline (X).—A mixture of benzalacetone phenylhydrazone (1 g.) and glacial acetic acid (3 cc.) was heated in an oil bath of 130° for 1 hour. Crystals (0.8 g.) separated on cooling were recrystallized from 13 cc. of methanol to give the desired product, yellow long prisms melting at 112–113°.[15]

1-Phenyl-3-methyl-5-(4-nitrophenyl)-2-pyrazoline (XI).—The crude product obtained similarly from 1 g. of the phenylhydrazone (IX) was three times recrystallized from ethanol, yielding 0.6 g. of apricot yellow needles, m. p. 113–113.5°.[16]

12) All temperatures are uncorrected.
13) Reported m.p. 157°. See E. Fischer, *Ber.*, 17, 576 (1884).
14) Reported m.p. 195-196°. See K. Auwers and H. Voss, *Ber.*, 42, 4425 (1909).
15) K. Auwers and H. Voss (loc. cit.) give m.p. 115-116°.
16) K. Auwers and H. Voss (loc. cit.) give m.p. 112-113°.

3-Methyl-5-phenyl-2-pyrazoline (XII).—Following the procedure of Beech et al.[11], 11 g. (67 %) of the desired pyrazoline, b. p. 140–142°/13 mm.[17] was obtained from benzalacetone (14.6 g.), 80 % hydrazine hydrate (11 g.), and ethanol (40 cc.).

3-Methyl-5-(4-nitrophenyl)-2-pyrazoline (XIII).—A mixture of 9.6 g. of 4-nitrobenzalacetone, 4 g. of 80 % hydrazine hydrate, and 20 cc. of ethanol was stirred at room temperature. As soon as the ketone dissolved, yellow precipitates[18] began to separate, but dissolved again to make a clear red solution, and then the whole slowly solidified on further stirring. The cake was filtered, washed with ethanol, suspended in 100 cc. of water and acidified with 10 % hydrochloric acid. The solution was filtered and neutralized partially with 10 % sodium hydroxide, forming a resinous orange substance which was filtered off. The filtered solution was made slightly alkaline to give cream yellow crystals, m. p. 98–100°. After a recrystalization from 20 cc. of ethanol, 6.6 g. (65 %) of the desired product, m. p. 97–102°, was obtained. Further recrystallization from ethanol gave an elevation of the melting point to 104–107° (Found: N, 20.60 %. Calcd. for $C_{10}H_{10}N_3O_2$: N, 20.58 %.). As this substance is likely to change to red resinous material, it is desirable to store it in sealed brown colored ampules.

1-Thiocarbamyl-3-methyl-5-phenyl-2-pyrazoline (XIV).—A mixture of 1.5 g. of benzalacetone, 1 g. of 80 % hydrazine hydrate, and 10 cc. of ethanol was refluxed gently on a water bath for 1 hour. After removing the ethanol under reduced pressure, the residue was mixed with ammonium thiocyanate (1.1 g.) and water (20 cc.). The whole was acidified with 10 % hydrochloric acid and the undissolved red oil was removed by filtration. The solution was then heated on a water bath for 5 hours to give yellow plates, m. p. 228–229° (decomp.), yield 0.5 g. (23 %). Recrystallization from ethanol changed the melting point to 230–231° (decomp.) (Found: N, 19.12 %. Calcd. for $C_{11}H_{13}N_3S$: N, 19.12 %).

1-Thiocarbamyl-3-methyl-5-(4-nitrophenyl)-2-pyrazoline (XV).—A mixture of 3-methyl-5-(4-nitrophenyl)-2-pyrazoline (2.1 g.), ammonium thiocyanate (1.1 g.), and water (40 cc.) was acidified with 10 % hydrochloric acid to pH 2.2 and an undissolved red tarry substance was removed by decantation. The solution was then heated on a water bath for 3 hours to form the desired product melting at 268–269° (decomp.), slightly orange yellow prisms (Found: N, 21.68 %. Calcd. for $C_{11}H_{12}N_4O_2S$: N, 21.20 %). Several recrystallizations from ethanol yielded faintly yellow prisms, m. p. 271° (decomp.).

1-(N-Phenylthiocarbamyl)-3-methyl-5-phenyl-2-pyrazoline (XVI).—Phenyl isothiocyanate[19] (1.4 g.) and 3-methyl-5-phenyl-2-pyrazoline (1.6 g.) were mixed and stirred at room temperature. The whole solidified immediately. The white solid was triturated with petroleum ether, filtered and washed with petroleum ether, to obtain the product, m. p. 166–167°, yield 2.8 g. On recrystallization from 200 cc. of methanol, there was obtained 2.1 g. (70 %) of colorless prisms, m. p. 160–161°. Further recrystallization from methanol did not change the melting point. (Found: N, 13.82 %. Calcd. for $C_{17}H_{17}N_3S$: N, 14.23 %).

1-(N-Phenylthiocarbamyl)-3-methyl-5-(4-nitrophenyl)-2-pyrazoline (XVII).—A solution of 3-methyl-5-(4-nitrophenyl)-2-pyrazoline (0.51 g.), and phenyl isothiocyanate (0.34 g.) in benzene (4 cc.) was allowed to stand at room temperature for several days. After removing benzene, reddish brown syrup was extracted with 25 cc. of ether and the ether extract was dried over anhydrous sodium sulfate. The ether was evaporated to form a red oil which changed to a glass-like solid after several days. The solid was extracted with 15 cc. of hot methanol and the methanol was removed to give crystalline residue. Recrystallization from methanol gave tiny slightly greenish-yellow needles melting at 141–142°, yield 0.33 g. (38 %). Further recrystallization elevated the melting point to 143–144° (Found: N, 16.41 %. Calcd. for $C_{17}H_{16}N_4O_2S$: N, 16.46 %).

1-(N-Benzoylthiocarbamyl)-3-methyl-5-phenyl-2-pyrazoline (XVIII).—Benzoyl chloride (4.2 g.) was added dropwise to a suspension of ammonium thiocyanate (2.4 g.) in acetone (24 cc.) and the whole refluxed gently for several minutes. To this reaction mixture was added dropwise a solution of 3-methyl-5-phenyl-2-pyrazoline (prepared from 1.5 g. of benzalacetone and 0.9 g. of 80 % hydrazine hydrate) in acetone. The content was refluxed for several minutes after the addition was completed and then poured into 200 cc. of water. Yellow crystals were collected, washed with water and recrystallized from ethanol. The yield was 2.2 g. (69 % based on benzalacetone), m.p. 185–185.5° (decomp.), greenish yellow plates (Found: N, 13.07 %. Calcd. for $C_{18}H_{17}N_3OS$: N, 13.00 %).

1-(N-Benzoylthiocarbamyl)-3-methyl-5-(4-nitrophenyl)-2-pyrazoline (XIX).—This compound was similarly prepared, yellow prisms (from acetone), yield 2.7 g. (73 %) from 2.2 g. of 3-methyl-5-(4-nitrophenyl)-2-pyrazoline, m. p. 199–200° (decomp.) Found: N, 15.41 %. Calcd. for $C_{18}H_{16}N_4O_3S$: N, 15.21 %).

1-Formyl-3-methyl-5-phenyl-2-pyrazoline (XX).—A solution of 1.7 g. of 3-methyl-5-phenyl-2-pyrazoline in 8 cc. of formic acid was heated for 1 hour on a water bath. Methanol was added to the reaction mixture and removed under reduced pressure. This procedure was repeated twice more to give a yellow oil. The oil was dissolved in 2 cc. of 25 % methanol and the methanol solution poured into 10 cc. of water. By rubbing the wall of the beaker a white precipitate was formed, which was filtered, and washed with water, m. p. 66–69°, colorless needles. This was recrystallized from 25 % methanol to yield 1.1 g. (55 %) of the desired product, m. p. 65–78° before drying, m. p. 88.5–89° after drying in a desiccator (Found: N, 14.75 %. Calcd. for $C_{11}H_{12}N_2O$: N, 14.89 %).

1-Formyl-3-methyl-5-(4-nitrophenyl)-2-pyrazoline (XXI).—3-Methyl-5-(4-nitrophenyl)-2-pyrazo-

17) S.G. Beech, et al. (loc. cit.) give b.p. 166°/35mm.

18) Intermediate formation of the precipitates was not observed when the reaction temperature was higher.

19) F. B. Dains, R. Q. Brewster and C. P. Olander, "Organic Syntheses", Col. Vol. I. p. 447 (1946).

line (1.1 g.) was dissolved in 5 cc. of formic acid and heated on a water bath for 1 hour. After removing the formic acid, methanol was added and removed under reduced pressure. This procedure was repeated once more to give dull orange yellow crystals. Recrystallizations from 25 % methanol gave a sample melting at 121–122°, yield 0.7 g. (60 %), pale yellow plates (Found: N, 18.05 %. Calcd. for $C_{11}H_{11}N_3O_3$: N, 18.02 %).

1-Acetyl-3-methyl-5-phenyl-2-pyrazoline (XXII).—A mixture of 1.7 g of 3-methyl-5-phenyl-2-pyrazoline, 2 cc. of acetic anhydride, and 10 cc. of water was stirred at room temperature. Colorless oil separated was extracted with ether (20 cc.) and the ether washed with water containing sodium hydroxide, with water containing hydrochloric acid and then with distilled water and dried over anhydrous sodium sulfate. Evaporation of ether at room temperature gave 1.1 g. of colorless crystals. On recrystallization from ether, there was obtained a sample melting at 77.5-78°.[20]

1-Acetyl-3-methyl-5-(4-nitrophenyl)-2-pyrazoline (XXIII).—

(a) A mixture of 0.5 g. of 3-methyl-5-(4-nitrophenyl)-2-pyrazoline and 2.5 cc. of glacial acetic acid was heated on a water bath. Duration of heating and yield were as follows: 1 hour, 0.17 g. (28 %); 3 hours, 0.21 g. (34 %); 5 hours, 0.28 g. (45 %); 8 hours, 0.25 g. (40 %). The crude product of m. p. 136–137° was dissolved in hot water and the filtered solution was allowed to stand for 1–2 weeks at room temperature, giving large yellow crystals melting at 138° (Found: C, 58.57; H, 5.67; N, 16.90 %. Calcd. for $C_{12}H_{13}N_3O_3$: C, 58.27; H, 5.30; N, 16.99 %).

(b) To a suspension of 3-methyl-5-(4-nitrophenyl)-2-pyrazoline (0.8 g.) in 5 cc. of water 0.8 cc. of acetic anhydride was added dropwise and with stirring. The precipitate was washed with water and with cold ether to remove the red gummy substance, giving yellow powder melting at 137–138°. Recrystallizations from ether gave the desired product of m. p. 137–139°.

20) Beech et al. (loc. cit.) give m.p. 77-79°.

Summary

The preparation is described of 3-methyl-5-phenyl-2-pyrazoline, 3-methyl-5-(4-nitrophenyl)-2-pyrazoline and their 1-phenyl, thiocarbamyl, N-phenylthiocarbamyl, N-benzoylthiocarbamyl, formyl, and acetyl derivatives which were to be tested for antituberculous activity.

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Radiometric Determination of Small Amounts of Antimony

By Tomitaro ISHIMORI and Kaoru UENO

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Dichlorobisethylenediamine cobaltic hexachlorostibinate, the insoluble precipitate obtained by adding *trans*-dichlorobisethylenediamine cobaltic chloride to a hydrochloric acid solution of quinquevalent antimony, was reported first by Pfeiffer and Tapauch[1] in 1906. The reaction can be written as

$$\underset{\left\{\begin{array}{l}\textit{trans}\text{-Dichlorobisethylene-}\\ \text{diamine cobaltic chloride}\end{array}\right.}{[Co(en)_2Cl_2]Cl} + (Sb^vCl_6)^- \longrightarrow \underset{\left\{\begin{array}{l}\text{Dichlorobisetylenediamine}\\ \text{cobaltic hexachlorostibinate}\end{array}\right.}{[Co(en)_2Cl_2]\,(Sb^vCl_6)} + Cl^-$$

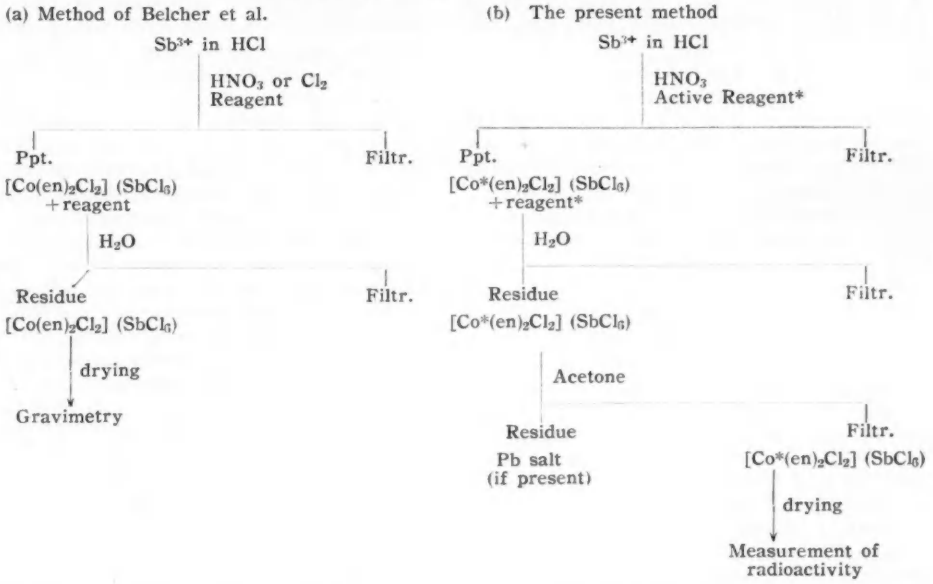
Recently Belcher and Gibbons[2] succeeded in gravimetric determination of antimony by means of the above-mentioned reaction. The scheme of the method is given in Table Ia. According to their paper, the lower limit of determinable amount is 1mg. antimony, and the determination is interfered with seriously with a very small amount of lead.

In the present paper, a radiometric method of determination of $(1-0.06)$ mg. antimony by radioactive *trans*-dichlorobisethylenediamine cobaltic chloride labelled with cobalt-60 is described. The present method consists of the precipitation of antimony and the washing with water according to the procedure given by Belcher et al. and the dissolution of the precipitate into acetone followed by the measurement of radioactivity. (Table Ib). Owing to the treatment with acetone in which antimony and lead salts are separated, this method is not disturbed

1) P. Pfeiffer und M. Tapauch, *Z. anorg. Chem.*, **49**, 438 (1906).
2) R. Belcher and D. Gibbons, *J. Chem. Soc.*, **1952**, 4775.

TABLE I

SCHEMES OF DETERMINATION OF ANTIMONY



even in the presence of small amounts of lead.

(1) Selection of Washing Solution and Solvent.—Before beginning the radiometric study, nonactive dichlorobisethylenediamine cobaltic chloride,[3] antimony and lead salts[4] of the complex are prepared and their behaviors against some kinds of organic solvents or mineral acids are checked.

The results are summarized in Table II.

TABLE II

BEHAVIORS AGAINST ORGANIC SOLVENTS AND MINERAL ACIDS

	Reagent	Sb salt	Pb salt
water	soluble	insoluble	partial decomposition
conc. HCl.	slightly soluble	insoluble	slightly soluble
hot dil. HNO_3	—	—	soluble with decomposition
acetone	insoluble	soluble	insoluble
ethyl alcohol	insoluble	slightly soluble	insoluble
ethyl ether	insoluble	slightly soluble	insoluble
chloroform	insoluble	slightly soluble	insoluble

3) W. C. Fernelius, "Inorganic Synthesis", Vol. II, McGraw-Hill Book Company, New York, N. Y. (1946), p. 222; Tupizina, dissertation, Zürich, 1912.

4) The antimony salt is prepared according to Belcher's method. The lead salt is prepared similarly from a saturated hydrochloric acid solution of lead nitrate. The composition of the lead salt is not known.

As can be seen from the table, the washing with water is suitable in separating precipitant and its antimony salt, and acetone is available to dissolve the antimony salt leaving the lead salt undissolved. These different behaviors against water and acetone are used as the basis of the following procedure.

(2) Radiometric Determination of (1—0.06) mg. Antimony.—Various amounts of antimony are taken and radioactive $[Co^*(en)_2Cl_2](SbCl_6)$ is precipitated; this is dissolved in acetone according to the following procedure. The relation between the relative intensity of the radioactivity of the residue of acetone extracts and the amounts of antimony taken is investigated.

(a) Preparation of the Radioactive Reagent.—Radioactive precipitant $[Co^*(en)_2Cl_2]Cl$ is prepared from radioactive cobalt chloride (about 0.2 milli curie Co^{60}/g. $CoCl_2 6H_2O$) according to the usual method[3], the heating to constant weight in an oven being omitted. This reagent is reserved in solid state to prevent the decomposition in an aqueous solution.

(b) Procedure.—1.5 cc. of the sample solution is taken in a microbeaker. The solution must be concentrated hydrochloric acid containing 1 to 0.06 mg. antimony. Three drops of concentrated nitric acid are added, and the solution is warmed for a few minutes and cooled quickly. In this treatment anti-

mony is oxidized to the quinquevalent state. 0.23 to 0.3 cc. Of a freshly prepared solution of the radioactive reagent (0.02 g. in 1 cc. of 2 N-hydrochloric acid) are added, and the mixture is set aside over night with occasional stirring. The precipitate is filtered off with a filter tube, washed with three or four portions of water until the washings become colorless, and dissolved in acetone. The acetone solution is transferred to a glass dish and evaporated under an infra-red lamp.

The radioactivity of the residue is measured by a Lauritsen electroscope, made by the Scientific Research Institute, Tokyo, and compared with that of a standard of cobalt-60.

TABLE III

RESULTS OF (2)

microg. Sb (taken)	Relative Intensity of Radioactivity, $(d/m)/(d/m)_S$	$(d/m)/(d/m)_S$ / microg. Sb.	% Deviation
0.0	0.000	—	—
67.0	0.180	2.69	−2.53
136.0	0.369	2.71	−1.81
199.9	0.527	2.64	−4.35
268.0	0.756	2.82	2.17
334.5	0.935	2.80	1.45
342.5	0.973	2.84	2.80
469.0	1.340	2.86	3.62
670.0	1.780	2.66	−3.62
682.0	1.910	2.80	1.45
945.0	2.660	2.81	1.81
	Mean	2.76	±2.57

The activity of the standard, $(d/m)_S$, is about $14d/m$. It shows slight variations according to the daily variation of the sensitivity of the Lauritsen electroscope.

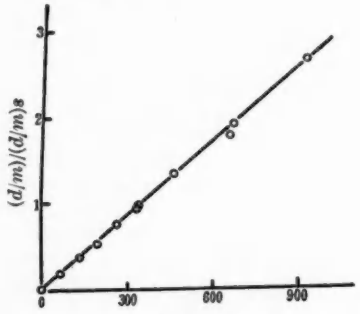


Fig. 1. Results of (2b).

(c) Results Obtained.—The results of experiments are shown in Table III and Fig. 1. The strictly linear relationship between the relative radioactivity and the amount of antimony taken is shown in Fig. 1, so we can conclude that 1 to 0.06 mg. antimony is determinable according to the above procedure.

If the reagent with much stronger specific activity is used, the determination of much smaller amounts of antimony may be successful. However it is so dangerous to handle the reagent of such high specific activity in solid state (as described above the reagent must be dissolved just before use). that we gave up such experiments.

(3) Determination of Antimony in the Presence of Lead.—Solutions which contain antimony as well as lead, are treated according to the procedure given in (2b). As can be seen from the results given in Table IV, the presence of a small amount of lead does not disturb the determination unless the ratio of lead to antimony is much less than one. However the errors are always negative and tend to increase as the ratio increases. Finally in two determinations in which the ratios are about one or more than one, errors become seriously negative.

TABLE IV

DETERMINATION OF ANTIMONY IN THE PRESENCE OF LEAD

microg. Pb (present)	microg. Sb (taken)	microg. Sb (found)	% Error
22.9	201	198	−1.5
22.9	201	199	−1.0
34.4	201	193	−3.9
114.5	397	394	−0.8
114.5	268	258	−3.7
114.5	130	95	−26.7
229	271	263	−2.9
229	268	261	−2.7
229	131	80	−39.1

Negative errors will be caused by the coprecipitated lead salt which prevents complete dissolution of antimony salt in acetone.

Roughly speaking, the present radiometric method is available in determining antimony in the presence of an almost equal amount of lead, while Belcher's gravimetric method is disturbed by 0.1 mg. lead in the determination of 23.74 mg. antimony.

The authors wish to express their hearty thanks to Professor Jun Yoshimura who was kind enough to read through the manuscript.

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Radiochemical Studies on Ultra-Micro Quantities of Organometallic Compounds. III. On Hydroxyquinolates of Promethium and Yttrium

By Tomitaro ISHIMORI

(Received November 11, 1953)

Hydroxyquinolates of promethium and yttrium have been studied using radioactive isotopes, promethium-147 and yttrium-90.

The formation of the hydroxyquinolates is confirmed by the facts that both promethium and yttrium are extracted from an aqueous solution into a chloroform solution of 8-hydroxyquinoline while they are not extracted by pure chloroform.

Further, some results are obtained on the composition of the complex compounds according to the method described in the first paper of these studies.[1]

(I) Promethium Hydroxyquinolate

So far there is no report on promethium hydroxyquinolate. The formation and composition of the complex salt are studied using promethium-147.

(A) The Solution of Promethium-147 Used.—Promethium chloride which was imported from the Oak Ridge National Laboratory, U. S. A., is diluted with hydrochloric acid (10% vol.). The resultant solution containing about 1.3 microcurie promethium-147 per cc. is used in the following experiments.

Radiochemical purity.—1 cc. of the solution mentioned above is evaporated up to measure the radioactivity of the residue through aluminum absorber of known thickness. The results are shown in Fig. 1, in which logarithms of the intensities (measured with a Lauritsen electroscope, made by the Scientific Research Institute, Tokyo, and given in divisions per minute) are plotted against thickness of absorber. From the figure we can guess that this radioactivity consists of two components, namely an alpha and a beta activity.

Thickness of absorber (mgAl/cm²)

Fig. 1. Absorption curve of "Promethium-149" (Semilog plot).

As contamination of plutonium is described on the certificate sent in the package of the solution of promethium-147, this alpha activity is considered to be due to plutonium.

The beta rays seem to be absorbed entirely by 45–50 mg. Al/cm². Substitution of this value in Glendenin's diagram[2] gives about 0.2 Mev. as the energy of the observed beta rays. This value coincides with that given by Friedlander and Kennedy[3] for the energy of radiation of promethium-147. Therefore, the solution of promethium used is considered to contain promethium-147 and some isotopes of plutonium.

In the following experiments, however, the activity is measured by a Lauritsen electroscope through an aluminum foil (about 8 mg. Al/cm²), so the contamination does not disturb the measurements of the activity of promethium. For this reason the separation of promethium from plutonium has not been tried.

(B) On the Formation of Promethium Hydroxyquinolate.—An aqueous solution (about 8–9 cc.) which contains 1 cc. of the solution of promethium-147 and 5 cc. of the solution of sodium potassium tartrate (5g./30 cc.) or the saturated solution of ammonium acetate is prepared. To adjust pH, ammonium hydroxide is added dropwise to the solution. The solution is made up to 10 cc. with water, and pH of the solution is checked with a pH test paper.

5 cc. of chloroform solution of 8-hydroxyquinoline (61 mg./50 cc.) are added to the aqueous solution and the mixture is shaken vigorously for one minute in a small separating funnel. The chloroform layer is taken and evaporated up under an infra-red lamp. The radioactivity due to promethium in the

1) T. Ishimori, This Bulletin, 27, 139 (1954).

2) L.E. Glendenin, *Nucleonics*, 2, 16 (1948).

3) cf. G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry", John Wiley & Sons, New York, (1949) p. 164.
ibid., p. 358.

residue is measured by the Lauritsen electroscope. The extractability is calculated by comparing the activity with that of promethium-147 taken into the separating funnel.

This procedure is repeated for several known pH values of the aqueous solution. The results are shown in Table I, in which

TABLE I

FORMATION OF PROMETHIUM 8-HYDROXYQUINOLATE

From the solution containing	pH	Extractability
Sodium potassium tartrate	9.2	23 %
,,	7.4	0.5
,,	3.4	...*
Ammonium acetate	5.6	0.4
,,	4.4	0.0

* tartaric acid is pptd.

we can see the remarkable transference of promethium into the phase of chloroform in the experiment at about pH 9. The similar procedure is repeated further with pure chloroform at about pH 9, but no promethium is extracted. So we may conclude that the formation of a new complex salt between promethium and 8-hydroxyquinoline at about pH 9 is proved by these experimental facts.

(C) On the Composition of Promethium Hydroxyquinolate.—The composition of the hydroxyquinolate is determined according to the method described in the first paper[1] of this series.

When a definite volume of an aqueous solution of promethium is shaken, at constant value of pH, with a known volume of a chloroform solution of 8-hydroxyquinoline until the equilibrium is established, the following equation is expected based on the theoretical consideration of the chemical system.

$$E^{-1}=A\,(\mathrm{HO}_x)^{-n}+B.$$

E: Extractability, the ratio of the activities due to promethium extracted and total promethium taken into the system.
(HO_x): The amount of 8-hydroxyquinoline added to the system.
A and B: Constants.
n: The number of the anion of 8-hydroxyquinoline bound to one atom of promethium.

Therefore, if several experiments are repeated with chloroform solutions of 8-hydroxyquinoline in varying concentration (keeping the other conditions constant) and their results are plotted in the E^{-1} $-(\mathrm{HO}_x)^{-1,2,3,\cdots}$ diagrams, n is determined by finding out $(\mathrm{HO}_x)^{-n}$ which is linear to E^{-1}.

(1) The Absorption of the beta Rays of Promethium.—In the experiments for the determination of the composition, precise measurement of the activity is earnestly desired. As promethium-147 is an emitter of considerably soft beta rays (0.20 MeV.), the absorption by 8-hydroxyquinoline which may come into the layer of chloroform must be considered.

Fortunately most 8-hydroxyquinoline seems to have been eliminated during the evaporation of chloroform solution under an infrared lamp. This is proved in two ways. The first is based on weighing the residue of chloroform solution of 8-hydroxyquinoline, namely the residue of 5 cc. solution (101 mg. 8-hydroxyquinoline/50 cc.) is less than 1 mg. Secondly, known volumes of the chloroform solution are evaporated in a glass dish containing the residue of 1 cc. of promethium solution and the radioactivity is measured. Table II shows the results in which we can

TABLE II

ABSORPTION OF BETA RAYS BY 8-HYDROXYQUINOLINE

mg. 8-hydroxyquinoline (added)	0.00	1.01	2.02	3.03	5.05	6.06	10.1
% Radioactivity	100	100	98	102	97	92	100

see that no serious error will occur by the absorption of the beta rays. The glass dishes used for measurements have a diameter of about 4 cm.

(2) Experimental Procedure.—A solution which contains 5 g. sodium potassium tartrate and 10 cc. of promethium-147 solution is made alkaline by adding ammonium hydroxide dropwise and finally made up to 100 or 50 cc. The pH value of the solution is checked by indicator paper. 10 cc. of the resultant solution is mixed with 5 cc. of a

TABLE III

RESULTS OF FIRST SERIES (pH=9.3)

(HO_x)	$(\mathrm{HO}_x)^{-1}$	$(\mathrm{HO}_x)^{-2}$	$(\mathrm{HO}_x)^{-3}$	$(\mathrm{HO}_x)^{-4}$	$(\mathrm{HO}_x)^{-5}$	E^{-1}
10 mg.	0.10	0.01	0.001	10^{-4}	10^{-5}	1.35
4	0.25	0.06	0.016	0.004	10^{-4}	3.78
3	0.33	0.11	0.037	0.012	0.004	6.88
2.7	0.37	0.14	0,051	0.019	0.007	11.6
2.4	0.42	0.17	0.073	0.030	0,013	16.4

TABLE IV
RESULT OF SECOND SERIES (pH=9.6)

(HO_x)	$(HO_x)^{-1}$	$(HO_x)^{-2}$	$(HO_x)^{-3}$	$(HO_x)^{-4}$	$(HO_x)^{-5}$	E^{-1}
10 mg.	0.10	0.01	0.001	10^{-4}	10^{-5}	1.23
4	0.25	0.06	0.016	0.004	10^{-3}	2.00
3.12	0.33	0.10	0.033	0.011	0.0034	3.23
2.68	0.38	0.14	0.055	0.021	0.0078	5.64

chloroform solution of 8-hydroxyquinoline (known concentration) and treated as described in (B). The procedure is repeated for several varying concentrations of 8-hydroxyquinoline in chloroform. Two series of experiments are carried out; the first is done at about pH 9.3 and the second is done at about pH 9.6.

(3) **Results Obtained.**—The results of these experiments are shown in Tables III and IV.

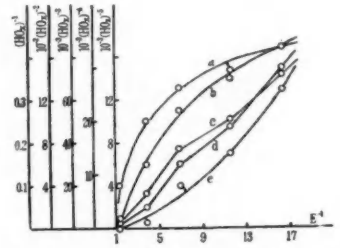

Fig. 2. Results of 1st series (pH=9.3).
a; $E^{-1}-(HO_x)^{-1}$, b; $E^{-1}-(HO_x)^{-2}$,
c; $E^{-1}-(HO_x)^{-3}$, d; $E^{-1}-(HO_x)^{-4}$,
e; $E^{-1}-(HO_x)^{-5}$,

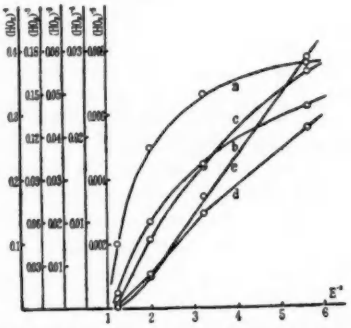

Fig. 3. Results of 2nd series (pH 9.6).
a; $E^{-1}-(HO_x)^{-1}$, b; $E^{-1}-(HO_x)^{-2}$,
c; $E^{-1}-(HO_x)^{-3}$, d; $E^{-1}-(HO_x)^{-4}$,
e; $E^{-1}-(HO_x)^{-5}$,

In Fig. 2 and 3 the diagrams of $E^{-1}-(HO_x)^{-1,2,3,4 \text{ and } 5}$ are given.

In these diagrams, figures of curve vary more slowly against the variation of n than in the cases previously reported by the author where the best linearity is got for $n=2$. So the determination of n becomes more difficult than the cases of lead dithizonate, lead hydroxyquinolate or polonium dithizonate.[1,4] Fig. 2a and b and Fig. 3a and b are clearly convex, and Fig. 2e and Fig. 3e are probably concave. So the best linearity is expected for $2<n<5$. However, we can not decide the value of n which gives the best linearity in E^{-1} vs. $(O_x)^{-n}$ diagram, because Fig. 2c and d and Fig. 3d are broken to a considerable extent. (We may assume that Fig. 3c is slightly convex.)

There is no generally accepted formula about the oxidation state of promethium in an aqueous solution, but according to its position in the periodic table, it belongs to the rare earth elements and it is most likely to assume trivalent cation of promethium. Based on this assumption, we can guess that the formula of the complex will probably be written as $Pm(O_x)_3$ or $Pm(O_x)_3(HO_x)$.[5] As the example of hydroxyquinolate of the latter type, thorium hydroxyquinolate, $Th(O_x)_4(HO_x)$, is known.[6]

(II) Yttrium Hydroxyquinolate

There is no description on yttrium hydroxyquinolate, except a report on its formation in an acetic acid solution[7]. In the present paper, the formation and composition of the complex salt of yttrium and hydroxyquinoline in chloroform medium, are studied using yttrium-90 which is easily prepared from strontium-90.

(A) **Preparation of Solution of Yttrium-90.**—Solution of "strontium-89" imported from the Oak Ridge National Laboratory, U.S.A., contains strontium-90. In the solution of "strontium-89" which has been left to stand for about 20 days, yttrium-90, the daughter element of strontium-90, is formed in an amount which is in equilibrium with strontium-90. Therefore, yttrium-90 can be isolated by the common chemical methods. Although a method for preparation of yttrium-90 based on radiocolloid of yttrium-90 was reported by G.K. Schweitzer et al.[8] a

4) T. Ishimori, This Bulletin, **27**, 520 (1954).
5) The concentration of undissociated 8-hydroxyquinoline in the aqueous solution is proportional to that of the anion of 8-hydroxyquinoline. Therefore, even in a case in which the complex salt is of the mentioned formula, the basis of the method is available.
6) F.J. Frere, *J. Am. Chem. Soc.*, **55**, 4362 (1933).
7) K. Shiba, *Rep. Gov. Chem. Ind. Res. Inst., Tokyo*, **28**, No. 8 (1932).

different method was used in the present research.

A solution of non-active strontium chloride (containing about 15 mg. strontium) is added to the solution which contains yttrium-90, strontium-90 and strontium-89 (about 0.5 milli curie strontium-90). After addition of ferric alum (0.1 g.), the resultant solution is made up to about 100 cc. and treated with ammonium chloride and ammonium hydroxide in order to coprecipitate yttrium-90 with ferric hydroxide. The precipitate is filtered off and reprecipitated according to the usual way.

Strontium goes to the filtrate and yttrium remains in the precipitate of ferric hydroxide. The precipitate is dissolved in hydrochloric acid (1 : 1) and iron is extracted into ether according to the Rothe's method. The aqueous solution which contains yttrium-90 is evaporated up and the residue is redissolved with water to obtain 25 cc. of the aqueous solution.

Ammonium chloride which is contained in the resultant solution does not disturb the result of the experiment.

Radioactivity of residue of the yttrium-90 solution thus prepared is strong enough (20–30 div./min. per cc.) for the following experiments and shows the decay as shown in Fig. 4. From the figure the half-life of the radio-

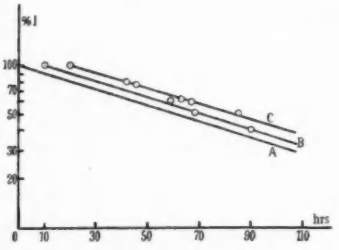

Fig. 4. Decay of Yttrium-90.
A : Theoretical decay for t=60 hrs.
B : Y-90 used in 1st series of experiments.
C : Y-90 used in 2nd series of experiments.

activity is calculated as about 60 hours, and this value almost coincides with that described by Friedlander and Kennedy[9].

As strontium has a long half-life (19.9 years), yttrium-90 is repeatedly prepared from the filtrate which contains strontium-90.

8) G.K. Schweitzer, B.R. Stein and Wm. M. Jackson, *J. Am. Chem. Soc.*, 75, 793 (1953).
9) G. Friedlander and J.W. Kennedy, "Introduction to Radiochemistry", John Wiley & Sons, New York, (1949) p. 327.

(B) On the Formation of Yttrium Hydroxyquinolate. -- An aqueous solution which contains 1 cc. of the solution of yttrium-90 and 5 cc. of the solution of sodium potassium tartrate (20%) or 5 cc. of ammonium acetate (20%) is treated in the almost same way as described in I, (B) and the extractability is calculated. This procedure is repeated for several different pH values of the aqueous solution.

The results are shown in Table V, in which

Table V
Extraction of yttrium hydroxyquinoline

Extraction of the complex from the solution containing	pH	Concentration of 8-hydroxyquinoline in $CHCl_3$ (mg./50 cc.)	Extractability
ammonium acetate	3.5	10	0.05%
,,	4.5	,,	0.1
,,	6.8	,,	0.15
,,	8.6	,,	3.6
,,	8.6	1000	53
sodium potassium tartrate	3.5	111	...*
,,	5.8	,,	0.0
,,	8.8	,,	28
,,	8.6	none	0.1
,,	8.8	,,	0.0

* Tartaric acid is pptd.

we can see that remarkable amounts of yttrium-90 are extracted from weak alkaline solution. Further similar procedure is repeated with pure chloroform at pH 8.6 and 8.8, but no yttrium is extracted. Basing our ideas on these facts, we can conclude that yttrium forms a hydroxyquinolate in an alkaline solution.

(C) On the Composition of Yttrium 8-Hydroxyquinolate.—The composition of yttrium hydroxyquinolate is estimated in a similar way as that described in I, (C). Two series of experiments are carried out at about pH 8.6 and 8.8.

The results of experiments are shown in Tables VI and VII. The $E^{-1}-(HO_x)^{-1,2,3}$

Table VI
Results of first series (pH=8.6)

(HO_x)	$(HO_x)^{-1}$	$(HO_x)^{-2}$	$(HO_x)^{-3}$	E^{-1}
1.0	1.0	1.0	1.0	1.78
0.4	2.5	6.3	15.6	11.9
0.2	5.0	25	125	40.3
0,12	8.3	69	578	100

(HO_x): Amount of 8-hydroxyquinoline given in an arbitrary unit in which $(HO_x)=1$ corresponds to 8.3 mg. 8-hydroxyquinoline.
E: Extractability.

TABLE VIII

RESULTS OF SECOND SERIES (pH=8.8)

(HO_x)	$(HO_x)^{-1}$	$(HO_x)^{-2}$	$(HO_x)^{-3}$	E^{-1}
11.1	0.09	0.008	0.0008	3.66
4.4	0.23	0.052	0.012	14.8
3.3	0.30	0.092	0.028	35.7
2.6	0.38	0.15	0.057	58.7
2.2	0.46	0.21	0.094	86.0

(HO_x): Amount of 8-hydroxyquinoline given in mg.
E: Extractability.

diagrames are given in Figs. 5 and 6. As

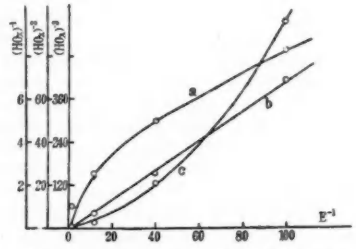

Fig. 5. Results of 1st series (pH=8.6).
a: $E^{-1}-(HO_x)^{-1}$, b: $E^{-1}-(HO_x)^{-2}$,
c: $E^{-1}-(HO_x)^{-2}$

can be seen in the figures, $(HO_x)^{-2}$ is linear to E^{-1}. So we can conclude that yttrium hydroxyquinolate contains 8-hydroxyquinoline anion in such a ratio as two anions are bound to one atom of yttrium. Consequently,

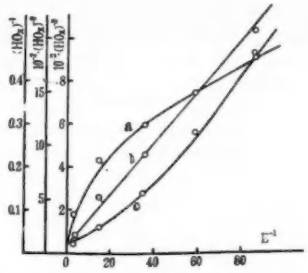

Fig. 6. Results of 2nd series (pH=8.6).
a: $E^{-1}-(HO_x)^{-1}$, b: $E^{-1}-(HO_x)^{-2}$,
c: $E^{-1}-(HO_x)^{-3}$

according to the results of the present study, we may guess that the composition of the complex salt will correspond to a formula such as $Y(O_x)_2X$, where (O_x) represents C_9H_6ON and X represents some monovalent anion other than $(O_x)^-$.

The studies of the complex in macro amounts is desired, because of possible differences between the composition of the complex compound formed from a concentrated solution and that formed from an extremly dilute solution.

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Studies on Dimethylglyoximato-cobalt (III) Complexes. II. Absorption Spectra of Bis-(dimethylglyoximato)-and Bis-(mono-O-methyl-dimethylglyoximato)-cobalt (III) Complexes*

By Akitsugu NAKAHARA

(Received October 21, 1954)

In the previous papers[1] the author discussed on the strong tendency of two dimethylglyoximate ions to form planar configuration about a cobalt atom, and attributed its origin to the formation of O–H–O hydrogen bonds in the complex radical. The successful synthesis of the tris-(dimethylglyoximato)-cobalt (III) reported in the same papers strongly supports the above conclusion. In order to confirm the conclusion, it might be suitable to compare properties of bis-(dimethylglyoximato)-cobalt (III) derivatives which have the O–H–O hydrogen bonds and bis-(mono-O-methyl - dimethylglyoximato) - cobalt (III) derivatives, in which the hydrogen bonds cannot be anticipated.

In this work, bis-(mono-O-methyl-dimethylglyoximato)-diammine-cobalt (III) chloride and hydrogen dinitro-bis-(mono-O-methyl-dimethylglyoximato)-cobaltate (III) were newly synthesized, and investigated spectrochemically. Absorption spectra of some bis-(dimethylglyoximato)-cobalt (III) complexes were

* The word "dimethylglyoximo-" was used in the former paper, but the above nomenclature seems to be better.

1) A. Nakahara, This Bulletin, **27**, 560 (1954); A. Nakahara and R. Tsuchida, *J. Am. Chem. Soc.*, **76**, 3103 (1954).

also investigated in relation to the above complexes of O-methyl-substituted dimethylglyoxime.

Experimental

Materials.- Bis-(mono-O-methyl-dimethylglyoximato)-diammine-cobalt (III) chloride, [Co$(NH_3)_2(DCH_3)_2$] Cl·1.5 H_2O.**[2]—This compound was prepared as reddish brown plates or prisms by the following method: 5 g. of purpureo cobalt (III) chloride, 5.2 g. of dimethylglyoxime-mono-methylether and 0.5 g. of charcoal were added to a mixture of 60 ml. of alcohol and 30 ml. of water, boiled for 10–15 hours on a water-bath, and then filtered. Alcohol was distilled off from the filtrate. The residual aqueous solution was evaporated and dried on a water-bath. The residue was washed once with chloroform and dissolved in alcohol. In this procedure only the objective complex was dissolved, and ammonium chloride was removed by filtration. When this dark brown filtrate was condensed in a vacuum desiccator on calcium chloride, the compound crystallized gradually. Analyses and other experiments for identification were already reported.[2]

Hydrogen dinitro-bis-(mono-O-methyl-dimethylglyoximato)-cobaltate (III), H [Co$(DCH_3)_2(NO_2)_2$].—This new compound was quantitatively precipitated from a hot solution of sodium hexanitrito-cobaltate (III) by careful addition of dimethylglyoxime-mono-methylether. The precipitate was almost pure after having been washed several times with hot water and alcohol. The compound did not show any reaction characteristic of sodium ion contrary to that showed by the dimethylglyoximato-complex obtained in the same procedure.[3] Found: C, 29.19; H, 4.61; N, 20.59, Calculated for H [Co$(DCH_3)_2(NO_2)_2$]: C, 29.27; H, 4.66; N, 20.48%. In order to determine the valency of cobalt, the magnetic susceptibility of the compound in solid state was measured, and it was necessarily concluded that cobalt should be tervalent since the compound proved to be diamagnetic. The compound appeared as orange, rhombic crystals. It is almost insoluble in water and alcohol, but dissolves a little in concentrated acetic acid. It explodes suddenly and burns on action of concentrated sulfuric acid.

Bis-(dimethylglyoximato)-diammine-cobalt (III) chloride, [Co$(NH_3)_2(DH)_2$] Cl·5H_2O.—This yellowish brown compound was prepared according to the direction of Nakatsuka and Iinuma.[4] As was already reported,[5] the crystal is of special interest in relation to its peculiar habit and unusual optical property.

Hydrogen dichloro-bis-(dimethylglyoximato)-cobaltate (III), H [Co$(DH)_2Cl_2$].[6]—The method of Cambi et al.[7] was applied in preparing the compound. To a concentrated aqueous solution of cobaltous acetate was added a slight excess of dimethylglyoxime, and the solution was oxidized by passing air through it. On adding concentrated hydrochloric acid, the compound was precipitated in dark green rhombs. It was recrystallized from the aqueous solution by adding concentrated hydrochloric acid.

Hydrogen dibromo-bis-(dimethylglyoximato)-cobaltate (III), H [Co$(DH)_2Br_2$].—The compound was precipitated in a similar way as the above described procedure from the reaction mixture by adding concentrated hydrobromic acid.

Chloro-bis-(dimethylglyoximato)-ammine-cobalt (III), [Co$(NH_3)(DH)_2Cl$]; Ammonium dinitro-bis-(dimethylglyoximato)-cobaltate(III), NH_4[Co$(DH)_2(NO_2)_2$]·H_2O; Nitro-bis-(dimethylglyoximato)-aquo-cobalt (III), [Co$(H_2O)(DH)_2(NO_2)$]; Nitro-bis-dimethylglyoximato-ammine-cobalt (III), [Co$(NH_3)(DH)_2(NO_2)$]; Hydrogen dinitro-bis-(dimethylglyoximato)-cobaltate(III), H [Co$(DH)_2(NO_2)_2$].—These complexes were prepared according to the direction of Tschugaeff.[3][8]

Dimethylglyoxime-mono-methylether. — Although there are some established methods concerning the syntheses of the compound,[9][10][11] a new method was adopted in this work: 7 g. of caustic soda and 20 g. of dimethylglyoxime were added to a mixture of 100 ml. of water and 200 ml. of alcohol, stirred and dissolved entirely on a water-bath. Into the mixture 25 g. of methyliodide was poured drop by drop during about half an hour with continuous stirring. The reaction mixture was boiled on the water-bath for two hours. Then alcohol was distilled off. On cooling the residual solution a white crystalline powder was deposited, which was filtered by suction, and purified by steam distillation. Thus 8.3 g. of pure dimethylglyoxime-mono-methylether (m.p. 104°C) was yielded, and 8.7 g. of unreacted dimethylglyoxime was recovered. By adding a large quantity of water to the distilled alcohol, dimethylglyoxime-dimethylether (m.p. 44°C) was also isolated.

Measurements. — Absorption spectra of the above compounds in solution were measured in the region from 40 to 135×10^{13}/sec. by a Beckman DU quartz spectrophotometer. The formal extinction coefficient ε is given by the equation $I=I_0\times10^{-\varepsilon cd}$, where c is the concentration of the complex in mol. or gram-ion per liter and d the thickness of the layer in cm. The concentrations used were $1/10^3-1/10^5$ and $1/10^2-1/10^4$ mol./l., in complexes and ligands, respectively. Absorption spectra of dichloro- and dibromo-complex were observed in water, as well as in methanol containing hydrochloric- and hydrobromic acid, respectively. Those of hydrogen dinitro-bis-(dimethylglyoximato)- and hydrogen dinitro-bis-(mono-

** $DCH_3=H_3CC(NOCH_3)C(NO)CH_3$; $DHCH_3=H_3CC(NOCH_3)C(NOH)CH_3$, $DH=H_3CC(NOH)C(NO)CH_3$; $DH_2=H_3CC(NOH)C(NOH)CH_3$.

2) A. Nakahara, Y. Yamamoto and R. Tsuchida, *J. Chem. Soc. Japan*, **74**, 1021 (1953).
3) L. Tschugaeff, *Ber.*, **41**, 2228 (1908).
4) Y. Nakatsuka and H. Iinuma, This Bulletin, **11**, 48 (1936).
5) Y. Saito, A. Nakahara and H. Kuroya, *J. Inst. Polytech.*, Osaka City Univ., **1**, No. 2, Ser. C, 15 (1950).
6) F. Feigl and H. Rubinstein, *Ann.*, **433**, 183 (1923).
7) L. Cambi and C. Coriselli, *Gazz. chim. ital.*, **66**, 81 (1936).
8) L. Tschugaeff, *Z. anorg. Chem.*, **46**, 144 (1905); *Ber.*, **39**, 2692 (1906); **40**, 3498 (1907); **41**, 2226 (1908).
9) G. Charrier, *Gazz. chim. ital.*, **37**, 145 (1907).
10) L. Avogadro and G. Tavola, ibid., **55**, 329 (1925).
11) E. Thilo, *Ber.*, **62**, 869 (1929).

O-methyl-dimethylglyoximato)-cobaltate (III) were also measured in 50% acetic acid, since they are almost insoluble in water as already mentioned. Absorption spectra of ligands, dimethylglyoxime and its methylether, were observed in alcohol. In cases other than the above, aqueous solutions were used.

Results and Discussion

Absorption Spectra of $[Co(NH_3)_2(DH)_2]Cl$, $[Co(NH_3)(DH)_2Cl]$ and $H[Co(DH)_2Cl_2]$. — The results of the measurements are shown in Fig. 1 and Table I. The three absorption curves are quite similar to each other except for the isolated maximum in the longer wavelength region on the curve of dichloro-complex, (c). As far as the absorption spectra of cobalt (III) complexes are concerned, there are, in general, two absorption maxima in the visible and near ultraviolet region.[12] The one in the visible has been designated as the "first absorption band", and the other in the near ultraviolet as the "second absorption band". According to Tsuchida, the first band is due to the electronic transitions in the unsaturated transition shell of the central ion and the second band is attributed to the transitions of the coördination electrons.[12][13] In the above complexes, however, the second bands are completely concealed by large absorption bands presumed to be the "specific absorption bands" which are due mainly to the dimethylglyoximate ions in coördination. Only the vestiges of the first bands remain slightly as inflations at $60\sim70\times10^{13}$/sec. in (a) and (b). The origin of dark or brownish colors which is characteristic of all Tschugaeff's dimethylglyoximato-complexes is attributed to the above mentioned facts. From this standpoint Feigl-Rubinstein's compound, $H[Co(DH)_2Cl_2]$,[5][7] having green color is a quite rare type of cobaltic complexes with dimethylglyoxime. Namely, the first band of this complex, (c), is nearly isolated from the specific band, showing its maximum at $\nu = 53.9\times10^{13}$/sec. The difference between (a), (b) and (c), however, is quite natural, considering the "spectrochemical series", an empirical rule found by Tsuchida.[12][13] Since the chloride ion is by far a more bathochromic ligand than the ammonia molecule in the series, the first band should be shifted bathochromically by substitution of the ammonia molecules by the chloride ions. On the other hand, Yamada and Tsuchida[14] recently presented another empirical rule, the "hyperchromic series" which is concerned with the intensity of the absorption of complexes. In the series, the ammonia molecule precedes the chloride ion, i.e., ammonia is a more hyperchromic ligand than the chloride ion. According to this rule, therefore, the relation between the first absorption bands of the three complexes can be explained also

TABLE I

ABSORPTION MAXIMA OF BIS-(DIMETHYLGLYOXIMATO)-COBALT (III) COMPLEXES

Notation	Complex radical	Solvent	First absorption band		Specific absorption band		Other bands		
			ν, 10^{13}/sec.	log ε	ν, 10^{13}/sec.	log ε	ν, 10^{13}/sec.	log ε	assignment
(a)	$[Co(NH_3)_2(DH)_2]^+$	water	—	—	123.0	4.41	—	—	—
(b)	$[Co(NH_3)(DH)_2Cl]$	water	—	—	122.0	4.38	—	—	—
(c)	$[Co(DH)_2Cl_2]^-$	CH_3OH-HCl	53.9	1.65	116.5	4.49	—	—	—
(d)	$[Co(DH)_2Cl_2]^-$	water	—	—	121.0	4.36	—	—	—
(e)	$[Co(DH)_2(NO_2)_2]^-$	water	—	—	122.0	4.44	87.6	3.86	nitro-groups
(f)	$[Co(NH_3)(DH)_2(NO_2)]$	water	—	—	123.0	4.40	—	—	—
(g)	$[Co(H_2O)(DH)_2(NO_2)]$	water	—	—	121.5	4.41	—	—	—
(h)	$[Co(DH)_2Br_2]^-$	CH_3OH-HBr	52.1	1.79	118.8	4.22	99.8	4.27	third band

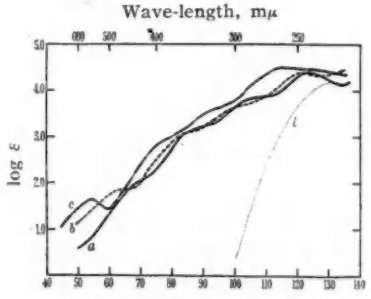

Fig. 1. Absorption spectra of: (a), $[Co(NH_3)_2(DH)_2]Cl$ in water; (b), $[Co(NH_3)(DH)_2Cl]$ in water; (c), $H[Co(DH)_2Cl_2]$ in 4% HCl-methanol.

12) See, for example, R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds" (in Japanese), (Zoshindo, Osaka, Japan, 1944).

13) R. Tsuchida, This Bulletin, **13**, 388 (1938).

14) S. Yamada and R. Tsuchida, This Bulletin, **26**, 15 (1953).

with respect to their intensities.

In the ultraviolet region, there can be recognized two inflations and one maximum. These may be considered to be the above mentioned specific absorption bands, since they are truly characteristic of dimethylglyoximato-complexes. Above all, in (a) and (b) the appearances of the absorption curves in the region are quite similar to each other, suggesting the same configuration of two dimethylglyoximate ions in each complex radical. As is clear from Table I, however, the maximum on the curve of dichloro-complex, (c), is shifted bathochromically, to a considerable degree. For this phenomenon some origins may be considered: (1) the effect of the two chloride ions coördinated in trans-positions[8]; (2) the solvent effect in methanol-hydrochloric-acid solution. It would probably be supposed that both the two effects are concerned in the above phenomenon. Further discussion will be given in the later section concerning the origins which contribute to the specific band.

Absorption Spectra of $NH_4[Co(DH)_2(NO_2)_2]$, $[Co(NH_3)(DH)_2(NO_2)]$ and $[Co(H_2O)(DH)_2(NO_2)]$.—The results of the measurements are shown in Fig. 2 and Table I. Absorption

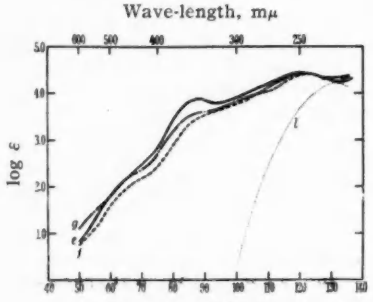

Fig. 2. Absorption spectra of aqueous solution of: $NH_4[Co(DH)_2(NO_2)_2]$, (e); $[Co(NH_3)(DH)_2(NO_2)]$, (f); $[Co(H_2O)(DH)_2(NO_2)]$, (g).

curves of these three complexes are quite similar to one another. Only the maximum at $\nu=87.6\times10^{13}$/sec. on the curve of dinitro-complex, (e), is conspicuous. This is the specific absorption band which is due to the nitro-groups in coördination.[15] Also on the curves, (f) and (g), the inflations higher than those of other complexes are recognized in this region. But they are not so remarkable as that of the dinitro-complex. This is due to the number of nitro-groups contained in the complex radical, since the specific absorption band usually changes hyperchromically with increasing number of the concerned ligands.[15] In the longer wave-length region, the vestiges of the first bands are almost unrecognized. But this may be understood by taking into consideration the above described intense specific band originating from the nitro-groups along with the hypsochromic shift of the first bands, which is also caused by the nitro-groups, one of the most hypsochromic ligand in the spectrochemical series. So far as the maxima in the shorter wave-length are concerned, there cannot be recognized any particular difference from the curves, (a) and (b), as is clear from Table I.

Absorption Spectra of $H[Co(DH)_2Br_2]$ and $H[Co(DH)_2(OH)Cl]$.—In Fig. 3 absorption

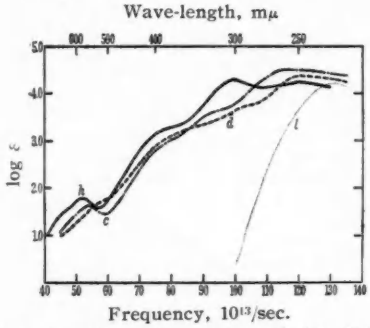

Fig. 3. Absorption spectra of: (d), H[Co(DH)$_2$Cl$_2$] in water; (h), H[Co(DH)$_2$Br$_2$] in 5% HBr-methanol.

curves of the above two compounds are illustrated. In the measurement of the former, (h), methanol-hydrobromic-acid solution was used, while in the case of the latter, (d), was adopted aqueous solution of the Feigl-Rubinstein's dichloro-complex, $H[Co(DH)_2Cl_2]$. It is because the dichloro-complex has been known to change itself into the above described chloro-hydroxo-complex in aqueous solution.[17] Although the valency of cobalt in the Feigl-Rubinstein's complex was considered previously to be bivalent, it is quite sure, by the investigation of Cambi et al[7], that it must be tervalent. Therefore, the above change should be elucidated according to the following scheme:

[8] It has been well-known that the third absorption band should appear readily when a central ion of a complex radical involves two anions in trans-positions. (Ref. 12). Consequently, there may be expected an overlapping of the third-and specific-band. In this case, such a bathochromic shift as above mentioned is very probable.

15) H. Kuroya and R. Tsuchida, *J. Chem. Soc. Japan*, **59**, 1142 (1938).

16) R. Tsuchida and M. Kobayashi, This Bulletin, **13**, 474 (1938).

17) "*Gmelins Handbuch d. anorg. Chem.*", 8 Aufl., **58 B**, p. 21 (1930).

$$H[Co(DH)_2Cl_2]+H_2O \rightleftarrows H[Co(DH)_2(OH)Cl]+HCl$$

As shown in Fig. 3 the curve, (d), is quite different from (c), suggesting the substitution of a ligand as presented in the above equation. Since the change is, however, in an equilibrium in aqueous solution, further discussion would be impossible without more detailed researches.

As for the absorption spectrum of the dibromo-complex, (h), all the explanations described in the case of the dichloro-complex, (c), can be applied. An important fact is that the bromide ion is a more bathochromic ligand than the chloride ion. In the present case, however, there can be recognized clearly a new maximum at $\nu=100\times10^{13}$/sec. This may be considered to be the third absorption band which is due to the two bromide ions coördinated in *trans*-positions, as is known in the absorption spectrum of *trans*-dibromo-bis-(ethylenediamine)-cobalt (III)-complex.[18]

Absorption Spectra of $[Co(NH_3)_2(DCH_3)_2]Cl$ and $H[Co(DCH_3)_2(NO_2)_2]$ in Relation to Those of $[Co(NH_3)_2(DH)_2]Cl$ and $H[Co(DH_2)(NO_2)_2]$.—The results of the measurements are shown in Fig. 4. The absorption curve of bis-

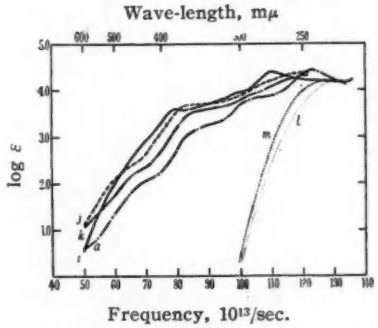

Fig. 4. Absorption spectra of: (i), $[Co(NH_3)_2(DCH_3)_2]$ Cl in water; (j), H $[Co(DCH_3)_2(NO_2)_2]$ in 50% acetic acid; (k), H $[Co(DH)_2(NO_2)_2]$ in 50% acetic acid; (l), dimethylglyoxime in alcohol; (m), dimethylglyoxime-mono-methylether in alcohol.

(mono-O-methyl-dimethylglyoximato)-diammine-cobalt (III) chloride, (i), resembles, as a whole, that of the corresponding dimethylglyoximato-complex, (a), but the former is considerably bathochromic to the latter.

Since dimethylglyoxime and its methylether are closely related in their electronic structures, it may be expected quite naturally that the curve, (i), would have a strong resemblance to the curve, (a). In fact, notwithstanding a little difference between the absorption maxima of the two ligands, (l) and (m), there is brought about a considerable difference when they are in coördination. (Table II). This can be understood by taking

TABLE II
SPECIFIC BANDS OF $[Co(NH_3)_2(DH)_2]Cl$ AND $[Co(NH_3)_2(DCH_3)_2]Cl$

	νmax, 10^{13}/sec.	log ε	ν max(complex) ~ ν max(ligand)
$[Co(NH_3)_2(DH)_2]Cl$	123.0	4.41	7.4
ligand, DH_2	130.4	4.20	
$[Co(NH_3)_2(DCH_3)_2]Cl$	110.3	4.37	17.9
ligand, $DHCH_3$	128.2	4.21	

the origin of the specific bands into consideration.

That is, the specific bands are the results of the polarizing deformation of the concerned ligands in the complex radical. While the two strong O-H-O hydrogen bonds are, as discussed in the previous paper,[1] expected in the bis-(dimethylglyoximato)-cobalt (III)-complexes, there could not be expected such hydrogen bonds in the corresponding bis-(mono-O-methyl-dimethylglyoximato)-complexes. Therefore, the degree of the polarizing deformation is anticipated to be larger in the latter than in the former. As for the reason of the above presumption, there may be supposed defying action of protons against the polarizing deformation of the concerned ligands under the effect of the cobalt (III) ion. In other words, the difference between the absorption spectra of $[Co(NH_3)_2(DCH_3)_2]Cl$ and $[Co(NH_3)_2(DH)_2]Cl$ supports the conclusion that the O-H-O hydrogen bonds play an important role in the determination of the electronic structure of bis-(dimethylglyoximato)-cobalt (III)-complex. The relation between the absorption curves of $H[Co(DCH_3)_2(NO_2)_2]$ and $H[Co(DH)_2(NO_2)_2]$ are similar to that between (a) and (i).

The Stabilities of Bis-(dimethylglyoximato)-complexes.—In the previous paper, it was concluded that the high stability of the bis-(dimethylglyoximato)-cobalt(III)-complexes, in which the two dimethylglyoximato ions coördinate to a cobalt atom with planar configuration, is attributed to the O-H-O hydrogen bonds in the complex radical. In this work, the above conclusion was confirmed by the other chemical evidence. Although bis-(mono-O-methyl-dimethylglyoximato)-diammine-cobalt (III) chloride can be prepared from purpureo cobalt (III) chloride according to the almost similar direction to that of the corresponding dimethylglyoximato-complex, the

18) M. Linhard and M. Weigel, *Z. anorg. Chem.*, 271, 101 (1952).

reaction for preparing the former is caused by the aid of charcoal and is finished less rapidly than that for preparing the latter. This indicates the fact that the bis-(dimethylglyoximato)-complex is by far more stable than bis-(mono-O-methyldimethylglyoximato)-complex. With respect to many other reactions for preparing bis(mono-O-methyl-dimethylglyoximato)-derivatives and corresponding dimethylglyoximato-derivatives, the above described conclusion is also supported. Such a distinct difference, which is originated from the substitution of the hydrogen atom by the methylradical will verify a remarkable contribution of O-H-O hydrogen bonds in the bis-(dimethylglyoximato)-complex radical towards the stabilization of the compounds. *Being united through the two O-H-O hydrogen bonds, the two dimethylglyoximate ions in the complex must be considered as one quadridentate group.*

Summary

Two new compounds, $[Co(NH_3)_2(DCH_3)_2]Cl$ and $H[Co(DCH_3)_2(NO_2)_2]$ have been synthesized as the first examples of tervalent-cobalt complexes of dimethylglyoxime-mono-methylether. Absorption spectra of the compounds and several bis-(dimethylglyoximato)-cobalt (III)-complexes in solution have been measured.

The absorption curves of bis-(dimethylglyoximato)-cobalt (III)-complexes, generally, consist of three inflations and one maximum. The inflation in the visible region is the vestige of the first absorption band, and the two other inflations and one maximum in the ultraviolet region are the specific absorption bands which are due mainly to the dimethylglyoximate ions in coördination.

As for the first absortion bands, the results of the measurements can successfully be elucidated on the basis of the spectrochemical- and hyperchromic-series found by Tsuchida et al. For $NH_4[Co(DH)_2(NO_2)_2]$, is also the specific band originated from the nitro-groups in coördination remarkable.

The isolated maxima on the curves of $H[Co(DH)_2Cl_2]$ and $H[Co(DH)_2Br_2]$ in the longer wave-length region are nothing but the first absorption bands which are shifted towards red owing to the bathochromic effect of the two halogenide ions.

In the dibromo-complex, the third absorption band is conspicuous. It has never been recognized clearly in the other complexes with dimethylglyoxime.

The absorption curves of bis-(mono-O-methyl-dimethylglyoximato)-complexes, as a whole, resemble those of corresponding dimethylglyoximato-complexes, but the bathochromic shift of the specific absorption bands from that of free ligand molecule amounts to a considerable degree in comparison with the cases of dimethylglyoximato-complexes. And this phenomenon is elucidated in connexion with the O-H-O hydrogen bonds.

From comparison of the reactions for preparing the bis-(mono-O-methyl-dimethylglyoximato)- and bis-(dimethylglyoximato)-complexes, the high stability of the latter was discussed.

The author wishes to express his sincere thanks to Professor R. Tsuchida and Dr. S. Yamada for their kind guidance and encouragement throughout this work. Appreciation is also expressed to Professor G. Hazato of the Tohoku University for the determination of magnetic susceptibilities. This study was supported in part by a grant from the Ministry of Education.

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*On the Specific Coloration of the Benzylamine Type Compounds in the Ninhydrin Color Reaction. I.**)

By Eiichi TAKAGI, Mitsuo MANGYO, Masanobu SAWAI and Isao ENSAKA

(Received September 10, 1954)

During the course of an investigation concerning reactions between aromatic aldehydes and α-amino acids[1], the authors noticed the specific coloration of the benzylamine type compounds with ninhydrin in paper chromatography.

We thought that if the amines have the following constitution, Ar–CH–R (Ar=Aryl group; R=H or Ar–CH–), yellow coloration will appear and then after an interval change to purple. Satake[2] pointed out a similar phenomenon, but details were not mentioned.

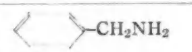
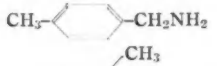
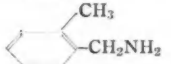
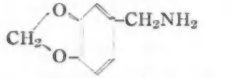
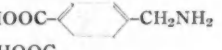
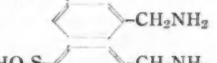
As the authors believed that this specific coloration could be a convenient and simple method for detecting a specific benzylamine-skeleton in a molecule, we studied several similar compounds and already published some of the results of the thesis[3].

Further studies were made on the same phenomenon using other substances and also using another reagent, alloxan. The present paper summarizes evidences obtained since the previous work.[1]

Coloration with Ninhydrin

The results with ninhydrin and alloxan color reactions are summarized in Table I.

TABLE I

No.	Ar-CH- type compounds (NH)	Specific ninhydrin color reaction	Specific alloxan color reaction	*Rf* value	Synthetic methods of the compounds*
1		+	+	0.65	E. Takagi et al[4]
2		+	+	0.71	F. Lustig[5]
3		+	+	0.71	H. Strassmann[6]
4		+	+	0.55	M. Tiffeneau[7]
5		+	+	0.64	E. Takagi[8]
6		+	+	0.62	E. Takagi[8]
7		+	+	0.58	F. F. Blicke et al[9]
8		+	+	0.50	A. Einhorn[10]
9		+	+	0.09	Sample No. 10 is hydrolysed with sulfuric acid.

* Continuation of the paper: E. Takagi and M. Mangyo, *J. Pharm. Soc. Japan*, **72**, 812-5 (1952).

1) loc. cit.

2) K. Satake, "Chromatography" (Kyoritsu Zensho) (1951), p. 88.

3) 6th Meeting of the Chemical Society of Japan, held at Kyoto on April 4, 1953.

4) E. Takagi, I. Ensaka, M. Mangyo and M. Sawai, *J. Pharm. Soc. Japan*, **73**, 1086 (1953).

5) F. Lustig, *Ber.*, **28**, 2988 (1895).

6) H. Strassmann, *Ber.*, **21**, 577 (1888).

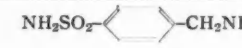
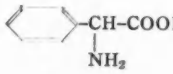
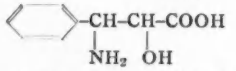
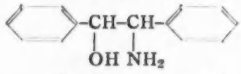
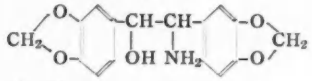
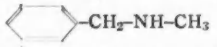
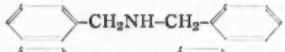
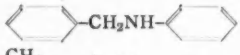
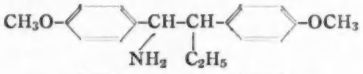
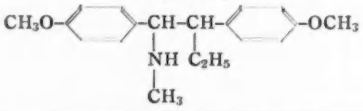
7) M. Tiffeneau, *Bull. soc. chim. France*, **9**, 823 (1911).

8) E. Takagi, *J. Pharm. Soc. Japan*, **71**, 656 (1951).

9) F. F. Blicke and W.M. Lilienfeld, *J. Am. Chem. Soc.*, **65**, 2281 (1943).

10) A. Einhorn, *Ann.*, **343**, 295 (1905).

TABLE I (Concluded)

No.	Ar-CH(NH)- type compounds	Specific ninhydrin color reacton	Specific alloxan color reaction	*Rf* value	Synthetic methods of the compounds*
10		+	+	0.37	Commercial substance made by the Wako Pure Chemical Industries, Ltd.
11		+	+	0.48	C.S. Marvel et al[11]
12		+	+	0.59	M.O. Forster et al[12]
13		+	+	0.81	E. Takagi et al[4]
14		+	+	0.74	E. Takagi[5]
15		+	+	0.70	E. L. Holmes et al[13]
16		+	+	0.67	A. Galat et al[14]
17		−	−	**	Org. Synth[15]
18		(+)	−	0.65	***
19		+	−	0.87	***
20		+	−	0.88	***

* Literature cited for the synthesis.

** Clear spot is not obtained.

*** We are indebted to Mr. T. Takahashi of the Department of Chemistry, Faculty of Science, Tokyo University, for these substances.

According to results obtained, with the exceptions of *p*-dimethylaminobenzylamine (18) and benzylaniline (17), all substances caused specific colorations on filter paper with ninhydrin, i.e., first yellow coloration which then changed to purple. *p*-Dimethylaminobenzylamine (18) developed at first an orange red color, but being comparatively stable, changed to purple very slowly. In the case of benzylaniline (17), we could not obtain a clear spot and moreover the color developed was purple-without passing the yellow stage, i.e., this substance resembled aniline in its behaviour.

In the samples of Table I, if the *p*-position of aminomethyl group is substituted with hydroxyl or methoxyl group, or 3,4-positions are substituted with methylenedihydroxyl group, the rate of color change was slow. This was especially so in the case of *p*-hydroxybenzylamine (4), which took a very long interval (few weeks) to change its color.

We can show other kinds of substances, too, which cause similar specific coloration with ninhydrins. The results with these other kinds of substance are summarized in Table II.

11) C.S. Marvel and W.A. Noyes, *J. Am. Chem. Soc.*, **42**, 2264 (1920).

12) M.O. Forster and K.A. RaO, *J. Chem. Soc.*, **1926**, 1947; K. Vogler, *Helv. Chim. Acta.* **33**, 2111 (1950).

13) E.L. Holmes and K. Ingold, *J. Chem. Soc.*, **127**, 1813 (1925).

14) A. Galat, and G. Elion, *J. Am. Chem. Soc.*, **61**, 3585 (1939).

15) Org. Synth., Vol. 8, 38 (1928).

TABLE II

No.	Substances	Specific ninhydrin color reaction	Specific alloxan color reaction	*Rf* value	Synthetic methods of substances
1	NH_2–CH_2CO–$NHCH_2COOH$[2)21)]	+	–	0.11	Commercial substance made by Wako Pure Chemical Industries, Ltd.
2	NH_2–CH_2–$COOC_2H_5$[2)]	+	–	0.52	T. W. Curtius[16)]
3	NH_2–CH(–CH_3)–$COOC_2H_5$	+	–	0.64	T. W. Curtius[16)]
4	$(CH_3)_2CH$–CH(NH_2)–$COOC_2H_5$	–	–	0.85	T. W. Curtius[16)]
5	CH_3–C(CH_3)(NH_2)–$COOC_2H_5$	–	–	—	A. L. Barker et al[17)]

Glycylglycine (1), glycine ethylester (2) and alanine ethyl ester (3) became yellow at first and then changed to purple.

Generally, the rates of the color changes of these substances in Table II are much greater than those of the substances in Table I.

Especially in the case of alanine ethyl ester (3), the color change occurred instantly. We could not find a yellow stage in the case of isoleucine ethyl ester (4) but it became purple directly, as normally occurs. Ethyl-α-aminoisobutyrate (5) gave no color with ninhydrin, which resembled that of the *tert*-butylamine[18)] due probably to lack of hydrogen atom where carbon atom is linked to the amino group.

Coloration with Alloxan*

As the intensity of coloration with alloxan was much weaker than that of the ninhydrin, we were obliged to change experimental conditions (cf. experimental). The results obtained are shown in the section of alloxan in Table I and II.

Generally, in the samples of Table I, the color first became yellow, then changed to orange in the middle stage and finally to a pink color. The relations between the rates of the color changes and the constitutions of the substances seemed to be similar to the tendency in the case of ninhydrin. However the yellow stage of α-aminophenylacetic acid (11) and β-amino-β-phenyl-lactic acid (12) were relatively long (about one day), being different from that of ninhydrin.

Contrary to the case of ninhydrin, the substances (Nos. 1, 2, 3 and 4) in Table II developed an orange or pink color directly without first passing through the yellow stage. Ethyl α-aminoisobutyrate (5) developed no color as in the case of ninhydrin.

Factors Affecting Color Change

We sought the factor affecting color change to solve the problem, i.e., what causes color change.

The results were:

(1) After having removed the specimens to a dark place at the first color stage, further color change took place.

(2) When kept in a vacuum desiccator, they did not change color but when they were brought into contact with air, they began to change color.

(3) When kept in an atmosphere of nitrogen gas with some water vapour, normal color change occurred.

(4) If the specimens were exposed to steam, the color change occurred very rapidly.

Accordingly, the rate of the color change is dependent on the degree of the humidity of air and to the chemical structure of the substances at a given temperature*. The mechanism of the color change will be discussed later[19)].

16) T.W. Curtius, *J. prakt. Chem.*, (2) 37, 159 (1888).
17) A.L. Barker and G.S. Skinner, *J. Am. Chem. Soc.*, 46, 405 (1924).
18) R. Moubasher and A. M. Othman, *J. Am. Chem. Soc.*, 72, 2666 (1950).
* We are indebted to Prof. K. Miyagi of the College of Pharmacy, Chiba University for this reagent.

19) Paper II. *J. Chem. Soc. Japan* (in press).
* When the samples were treated with water, the color change occurred comparatively slowly, showing that the rate of color change is affected by temperature.

Experimental

I. On the Paper Chromatography.—The authors carried out the paper chromatography in the usual manner. Details are as follows.

Sample: 0.5% aqueous solutions of the amino-carboxylic acids or the amino sulfonic acid. In the case of amines, 0.5–1% aqueous solutions of their hydrochlorides.

1/1000 cc. of the samples are spotted on the filter paper at the point, 3 cm from the end.

Filter paper: Toyo Roshi No. 2, 2 cm×20 cm.

Developing method: One dimensional ascending method.

Developing solvent: Mixture of *n*-butanol, acetic acid and water (4:1:1).

Developing temperature and time: 15–18°C, 3–4 hrs.

Developing distance to the solvent front from the original point: 13–15 cm.

Reagent: 0.2% ninhydrin solution in *n*-butanol.

In the case of alloxan the coloration was very weak as mentioned before, so we examined the color reaction by spot tests on filter paper using 0.5% alloxan solution in *n*-butanol.

II. On the Factor Affecting Color Change.—We prepared five series of the same specimens of a substance to seek the factor affecting color change and examined their behaviours as follows.

Samples: The positive substances of the specific color reaction in the Tables I and II were used. The tests of the special substances, which took a very long time or a very short time for the color change, were excluded.

Filter paper: Toyo Roshi No. 2.

Reagents; 0.2% ninhydrin and 0.5% alloxan solutions in *n*-butanol.

Color tests:

A) Ninhydrin test.—0.01 cc. of a sample was spotted in the same manner on five filter papers, airdried, sprayed with the ninhydrin reagent, and heated on an electric heater to develop the yellow color.

The five yellow colored specimens were examined for five series of the following tests.*

The first series of the specimens was kept in room air for control. The second was kept in a desiccator at an atmospheric pressure filled with air on calcium chloride and the third in an evacuated desiccator on concentrated sulfuric acid.

The fourth series was kept under an atmospheric pressure filled with nitrogen gas on some water, using a vacuum desiccator as the vessel, and the fifth was enclosed in a piece of black paper and was kept in a dark place.

We observed that the color change of the first series took place relatively rapidly (in several minutes to several hours); the second series caused slight color change in 100 hours, yellow-brown to brown but not to purple; the third series maintained its yellow to yellow-brown color for 100 hours; the fourth and the fifth series were similar to the first series, changing their color rapidly.

We could not observe remarkable differences among the first, the fourth and the fifth series.

B) Alloxan test.—In the case of the alloxan reagent, although the color changes were not identical to that of the ninhydrin, being orange in the middle stage in general, results obtained were similar. In the cases of both the ninhydrin and alloxan tests, when the specimens of the second and the third series were brought out to room air, they began to change their color in the normal manner, i.e., in ninhydrin, the color stabilized to purple and in alloxan, the color stabilized to pink.

When the specimens of the first color stage or the middle color stage were exposed to steam, they changed their color very rapidly to the stabilizing color.

The authors wish to acknowledge the support of Dr. F. Nagasawa, The Director of the Laboratory.

Summary

The specific coloration of the benzylamine type compounds in the ninhydrin color reaction is extended to other kinds of compounds. Alloxan resembles ninhydrin in its behaviour as reagent. The fact that the specific coloration reaction seems to be common to the benzylamine type compounds, is verified.

However a few exceptions are observed as in the case of benzylaniline (17) and *p*-dimethylaminobenzylamine (18). The fact that the color change of these compounds in the usual paper chromatography is due to moisture in the air, is confirmed.

Research Laboratory, Mitsubishi Chemical Industries Ltd.
Kawasaki, Kanagawa

20) Akabori and Narita, *Seni Kagaku Kenkyusho Nenpo*, **5**, 76 (1950).

* The room temperature was about 26°C and the humidity of the air was about 70%.

Solvent Effects on Ion Exchange Equilibria. Part I.

By Tomohiko SAKAKI

(Received September 27, 1954)

Introduction

It has been found that the addition of non-electrolytes to the ion exchange system generally causes shifts in equilibrium, which depend on the composition of the solvent system, the ionic species, etc. These effects have been studied in detail from the physico-chemical point of view, and some noticeable regularities have been found, thus suggesting that simple and well-defined procedures may be added to the list of ion exchange techniques.

The fact that only a few papers on this subject have as yet been published indicates that this aspect has been somewhat overlooked in the past. Some decades ago Wiegner et al[1] studied the ion exchanges between a calcium zeolite and various alkali chlorides dissolved in aqueous ethanol, and observed that more alkali ions passed into the exchanger as the concentration of ethanol was increased and that the exchange became nearly equal for all ions at higher concentrations of alcohol. The problem remained untouched until a recent investigation by Kressman and Kitchener[2]; they studied the effect of the addition of an organic solvent on the exchange of alkali ion, using a phenol-sulfonate resin. It was found that with the calcium resin-alkali salt system in aqueous ethanol the logarithm of the equilibrium constant increased linearly with the ethanol percentage, whereas with the $NH_4^+-K^+$ system in aqueous acetone the equilibrium constant itself changed linearly with the acetone concentration. More recently Okuno, Honda and Ishimori[3] investigated the exchange of alkali ions by sulfonated styrene type resins (H-form) in aqueous solutions containing various quantities of methanol or ethanol. They observed that the difference in the equilibrium constants of various alkali ions became greater as the alcohol concentration was increased. Their results have been reconfirmed by the more detailed study of the same system carried out in our laboratory under the collaboration of Kakihana and his co-workers.

A short note on our results has already been published[4] and the application of these to analytical and preparative chemistry has been discussed elsewhere.[5] Therefore the present paper will be limited to the physico-chemical treatment of the problem.

Experimentals and Results

(i) Properties of the Resin Used.—Amberlite IR-120 was used. Conventional techniques were employed for the conversion of the resin to the H-form, regeneration, determination of the exchange capacity per gram of dry resin, etc.

When the H-resin granules, which had been dried at 100°C under 15 mm Hg to constant weight, were allowed to absorb water vapor at 100 per cent relative humidity at room-temperature during ten days, it uptook 0.9 gram of water per gram of dry resin. To determine the exchange capacity of the resin, 0.1N solutions of potassium chloride in water, and 20, 40, 60, 80 and 100 per cent methanol or ethanol were used. This was found to be 5.10 ± 0.02 meq. per gram of dry resin, independent of the alcohol concentration of the solution used, that is, the total capacity was uninfluenced by the addition of alcohol.

(ii) Experimental Procedures.—The measurements were carried out under the following conditions. The alkali chloride was dissolved in the aqueous solution containing a known amount of alcohol, to yield 0.05, 0.1, or 0.2N salt/l. solutions. An adequate amount of the H-resin was added to 50 ml. of the salt solution, and subsequently the vessel containing the exchange system was kept shaken at 25 ± 0.05°C until the equilibrium had been attained. An aliquot portion of the solution was then analyzed for the hydrogen ion. The mole ratio of an alkali ion to hydrogen ion in the resinous phase at equilibrium was kept around unity by varying the quantity of the resin added. To avoid error due to the instability of the H-resin, the exchange capacity of the resin sample was simultaneously determined with each measurement of the exchange equilibrium.

(iii) Apparent Equilibrium Constant.—The exchange reaction involving metal ion M^+ and hydrogen ion H^+ is written as,

$$M^+ + HR = H^+ + MR.$$

The apparent exchange equilibrium constant, K_H^M, is given by

$$K_H^M = \frac{[H^+]\,[MR]}{[M^+]\,[HR]} \qquad (1.1)$$

1) G. Wiegner and H. Jenny, *Kolloid-Z.*, **42**, 268 (1927).
2) T. R. E. Kressman and J. A. Kitchener, *J. Chem. Soc.*, **1949**, 1211.
3) H. Okuno, M. Honda and K. Ishimori, *Bunseki-Kagaku* (*Japan Analyst*), **2**, 430.
4) T. Sakaki and H. Kakihana, *Kagaku* (*Science*), **23**, 471 (1953).
5) H. Kakihana, Chemical Industry (Kagaku Kogyo), Symposium Kogyo-Keisoku.

TABLE I

EFFECT OF ALCOHOL (25°C)

Salt	Conc. (N)	Alkali chloride−H-resin (Amb. IR-120)				
LiCl	0.2	Wt. % of methanol	0	30.0	50.0	
		K_H^{Li}	0.84_4	1.45	2.15	
	0.1	Wt. % of ethanol	0	21.8	36.7	40.5
		K_H^{Li}	0.80_3	1.32	2.18	2.37
NaCl	0.05	Wt. % of methanol	0	13.5	29.5	47.0
		K_H^{Na}	1.70	2.86	5.07	10.7
	0.2	Wt. % of ethanol	0	14.0	32.0	
		K_H^{Na}	1.84	3.33	8.15	
KCl	0.1	Wt. % of methanol	0	13.5	21.5	
		K_H^{K}	3.61	4.74	6.65	
	0.2	Wt. % of ethanol	0	14.0	34.0	
		K_H^{K}	3.74	5.25	17.8	

The mole ratio, $[MR]/[HR]$, was kept at 0.85–1.10 for Li^+ and Na^+, and at 1.86–2.30 for K^+.

where the bracket [ ] represents the analytical concentration of each species in eq./l.

The equilibrium measurements were carried out with 0.2N, 0.1N and 0.05N alkali chloride solutions containing various amounts of alcohol. A part of the results is given in Table I as typical data illustrating the solvent effects. It is to be noted that the following features may be deduced from these results.*) First, for the same metal ion and for the equal content of alcohol, K_H^M is always greater in aqueous ethanol than in aqueous methanol; secondly, the value of K_H^M becomes higher as the alcohol concentration is increased, and finally, the sequence of the magnitude of K_H^M is $K^+ > Na^+ > Li^+$, provided that the alcoholic solutions are of identical concentration.

Discussion

(i) The Free Energy Change of Ion Exchange and the Dielectric Constant of Solution.—In the system of aqueous alkali chloride solution and the sulfonic acid exchanger, it has been found by Boyd, Schubert and Adamson,[6] and ascertained by Kressman and Kitchener[7] that the apparent free energy change**) accompanied by ion exchange is inversely proportional to the hydrated radius of the exchangeable ion. This regularity is conveniently represented by the following equation;

$$-\Delta F'_{MR} = RT \ln K_H^M, \qquad (1.2)$$

$$= B + \frac{C_m}{D_s \cdot a_M} \qquad (1.3)$$

where $-\Delta F'_{MR}$ represents the apparent free energy change, B and C_m are constants, and D_s and a_M are the dielectric constant of solution and the hydrated radius of M^+ ion, respectively.

Fig. 1-1. shows the graph of $-\Delta F'_{MR}$ against

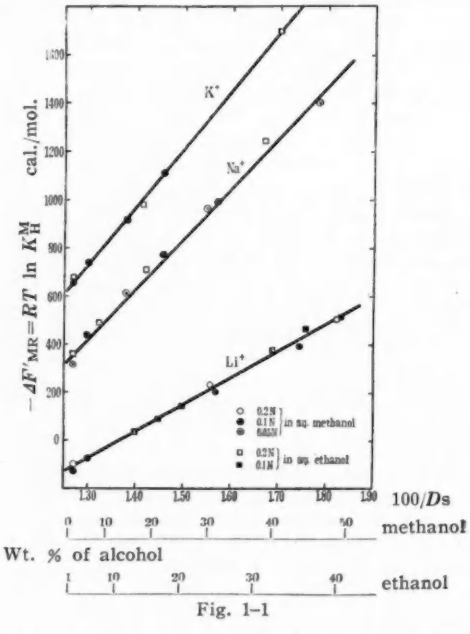


Fig. 1-1

$1/D_s$ for each ion. The values of $-\Delta F'_{MR}$ have been calculated from the data according to Eq. (1.2). Since the salt concentration is too low to give a notable influence on the values of D_s, they have been estimated from the alcohol concentrations of solutions, using results from macroscopic measurements.[8]

* See also the data given in reference 3).

6) G. E. Boyd, J. Schubert and A. W. Adamson, *J. Am. Chem. Soc.*, **69**, 2818 (1947).

7) T. R. E. Kressman and J. A. Kitchener, *J. Chem. Soc.*, **1949**, 1190.

** The free energy which these authors have used is nearly equal to the apparent free energy.

8) G. Åkerlöf, *J. Am. Chem. Soc.*, **54**, 4125 (1932).

This manner of plotting apparently gives a straight line for each ion in the range of $D_s > 55$. In order to let Eq. (1.3) represent the linear relationship between $-\Delta F'_{MR}$ and $1/D_s$, a_M must be kept invariable through the region of D_s in Fig. 1-1. It might be possible that owing to the preferential hydration of the ion the value of a_M is essentially uninfluenced by the addition of alcohol up to a concentration of 40 or 50 per cent in weight. When the alcohol content is increased and consequently the reciprocal of D_s exceeds the region shown in Fig. 1-1 the free energy vs. $-1/D_s$ curve, losing the linearity, reaches a maximum and falls sharply as $1/D_s$ approaches the value of absolute alcohol, as illustrated in Fig. 1-2.

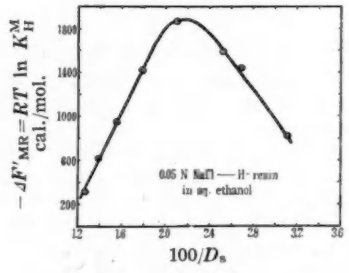


Fig. 1-2

This fact leads us, as the natural consequence, to the viewpoint that the ion may gradually lose its apparent affinity for water molecules in higher alcohol concentrations.

Furthermore it is to be noted that the slope of the line shown in Fig. 1-1 is characteristic to each ion and indifferent to the kind of coexisting alcohol, and that, as is expected from Eq. (1.3), the order of its magnitude is $K^+ > Na^+ > Li^+$, which is equal to the sequence of the value of K_H^M or $-\Delta F'_{MR}$ in aqueous solution. It goes without saying that these results are consistent with the observations stated in section II (iii).

(ii) **The Effect of Urea.**—It is interesting to examine the effect caused by the addition of non-electrolytes, such as urea, which contrary to the case of alcohol, increase the dielectric constant of solution.

According to Eq. (1.3) the value of K_H^M is expected to decrease with the addition of urea. This is supported by the results listed in Table II, which illustrates the data on the

TABLE II

EFFECT OF UREA (25°C)

0.1N NaCl—H-resin

(Amberlite IR-120)

Conc. of urea (Wt. %)	K_H^{Na}
0	1.68
0.8	1.31
1.6	0.93
2.4	0.77
3.2	0.70
4.0	0.44
6.0	0.37

system of Amberlite IR-120 and urea in 0.1N sodium chloride at 25°C. Though Eq. (1.3) seem to coincide with the facts in this case as well, close examination reveals that the agreement of the equation with experiments is only qualitative. If the data on D_s of aqueous urea solutions[9] are inserted into Eq. (1.3), the constants of which have beeen determined from Fig. 1-1, then, the value of K_H^M is found to be by far greater than that observed, that is, K_H^M appears to be more sensitive to the presence of urea than to that of alcohol. This discrepancy may be formally eliminated by admitting that the gradient C_m in Eq. (1.3) is generally dependent on the species of the non-electrolyte added, so far as a_M can not be assumed to decrease rapidly with the concentration of urea. But it must be taken into consideration that this simple empirical equation is inadequate for quantitative usage, since it lacks sufficient theoretical basis.

In conclusion, Eq. (1.3) represents semiquantitatively the effect of the addition of non-electrolytes on ion exchange equilibria. However, this cannot correlate successfully the free energy change with the valency of the exchangeable ion. Hence, further work is necessary to establish a relationship, which is not only consistent with the mentioned facts but also more generally applicable; this will be attempted in the ensuing paper.

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9) J. Wyman Jr., *J. Am. Chem. Soc.*, **55**, 4116 (1933).

Solvent Effects on Ion Exchange Equilibria. Part II.

By Tomohiko SAKAKI

(Received September 27, 1954)

In the preceding paper[1] it was pointed out that a semi-quantitative relationship exists between the free energy change of univalent ion exchange and the dielectric constant of the solution. The present paper is concerned with a more general regularity which governs the solvent effects on the exchange of polyvalent ion.

The Free Energy Change of Univalent Ion Exchange

The present discussions are limited, for simplicity, to the case in which the exchange groups of resin have the same ionization constant. Then, the free energy change, ΔF°, for the reaction of the type

$$M^+ + HR = H^+ + MR$$

is written

$$RT \ln K_a = -\Delta F^\circ, \qquad (2.\ 1)$$

where K_a is the thermodynamic equilibrium constant and is expressed as

$$K_a = K_H^M \cdot \frac{f_H \cdot f_{MR}}{f_M \cdot f_{HR}} \qquad (2.\ 2)$$

where f_i shows the activity coefficient of i species. Now let us specify by the symbol $(X)_o$ the value of the quantity X to be measured in aqueous solution—resin system, and by $(X)_m$ that in the system of aqueous alcohol—resin; then, from Eqs. (2. 1) and (2. 2), we get

$$(\Delta F'_{MR})_o - (\Delta F'_{MR})_m = (\Delta F^\circ)_o - (F^\circ)_m - RT\left\{\ln \frac{(f_H)_m}{(f_H)_o} - \ln \frac{(f_M)_m}{(f_M)_o}\right\} - RT\left\{\ln \frac{(f_{MR})_m}{(f_{MR})_o} - \ln \frac{(f_{HR})_m}{(f_{HR})_o}\right\} \qquad (2.\ 3)$$

The second term on the right-hand side of the above equation is readily evaluated by the Debye-Hückel theory, assuming that the solvated radii are kept constant indifferently of the addition of alcohol. The result of the calculation shows that this term contributes only a little to the total value of the difference in $-\Delta F'_{MR}$ shown in Fig 1-1 of the preceding paper.

It is difficult to estimate, without any assumption, the value of the third term, but it does not seem to be so unreasonable to assume that under the present experimental conditions this term is not so great when compared with the preceding term.

Thus,

$$(\Delta F'_{MR})_o - (\Delta F'_{MR})_m \approx (\Delta F^\circ)_o - (\Delta F^\circ)_m, \qquad (2.\ 4)$$

or

$$RT \ln \frac{(K_H^M)_m}{(K_H^M)_o} \approx RT \ln \frac{(K_a)_m}{(K_a)_o} \qquad (2.\ 5)$$

A Simple Model of Ion Exchange

Let us consider the free energy change of ion exchange, based upon a simple model. When an ion is brought into the resin phase and is fixed, either loosely or tightly, by one of the ionic groups, the solvent molecules attached to the ion may be more or less detached from it; the ion fixation may be accompanied by the desolvation process to a certain extent. This process can be analyzed into the three steps shown in Fig. 2-1. Step 1 represents the partial desolvation of ion in the solution having Ds; the ion enters the resin phase through step 2; and in step 3 the charge of the ion is neutralized by an ionic group of the opposite sign. Each step is accompanied by the free energy change ΔF_1, ΔF_2 and ΔF_3, respectively. It seems that among these free energy changes the second and the third do not vary with the species of exchangeable ion, that is, it is likely that the difference in the resultant free energy change between a pair of exchangeable ions is predominantly determined by that in the magnitude of ΔF_1.

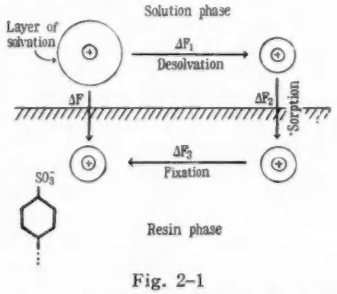

Fig. 2-1

The work of step 1 may be essentially of an electrical nature, so that, as a rough ap-

1) This Bulletin, **28** 217 (1955).

proximation, it can be regarded as being proportional to the solvation number of the ion and inversely proportional to the dielectric constant of the medium.

If the solvation number is tentatively replaced by the hydration number in the case of the solution of the lower alcohol concentration, we obtain the following equation as the final result of the above considerations;

$$(\Delta F^\circ)_o-(\Delta F^\circ)_m=C_n\cdot(n_H-n_M)\cdot\left\{\frac{1}{(D_s)_m}-\frac{1}{(D_s)_o}\right\}, \quad (2.6)$$

where n_H and n_M are the hydration numbers of hydrogen ion and metal ion, and C_n is a constant which depends upon the species of the solvent added and that of the resin used.

Combining Eqs. (1. 2), (2. 4) and (2. 6),

$$RT\ln\frac{(K_H^M)_m}{(K_H^M)_o}\approx C_n(n_H-n_M)\cdot\left\{\frac{1}{(D_s)_m}-\frac{1}{(D_s)_o}\right\}. \quad (2.6)$$

or, in general

$$RT\ln K_H^M\approx B+(n_H-n_M)\cdot\frac{C_n}{D_s}, \quad (2.8)$$

where $B=C_n(n_H-n_M)/(D_s)_o$.

Here the hydration numbers of exchangeable ions are adopted as parameters in place of their hydrated radii in Eq. (1. 3). When the values proposed by Stokes and Robinson[2] are introduced for n_H and n_M, it is readily found that Eq. (2. 8) agrees with the experimental results, obtained in the case of univalent ion exchange.

Polyvalent Ion Exchange

The apparent equilibrium constant K_H^M for the exchange reaction of the type

$$M^{z+}+zHR^+=zH^++MRz$$

is written as

$$K_H^M=\frac{(H^+)(MR_Z)^{1/2}}{(M^{z+})^{1/Z}(HR)}\cdot\left\{\frac{v}{V}\right\}^{\frac{z-1}{z}} \quad (2.9)$$

where z is the valency of metal ion, V and v are the volume of the solution and that of the solvent in the resin phase accessible to the ion in it, respectively, and ( ) represents the absolute quantity (equivalent) of each species found in each phase.

From Eq. (2. 9)

$$RT\ln K_H^M=RT\ln\frac{(H^+)\cdot(R_ZM)^{1/Z}}{(M^{z+})^{1/Z}(RH)}+\left\{\frac{z-1}{z}\right\}RT\ln\left\{\frac{v}{V}\right\}. \quad (2.10)$$

If the same consideration as in the case of univalent ion exchange is applied to this case, it leads us to

$$RT\ln K_H^M\approx B+(n_H-n_{M/z})\frac{C_n}{D_s}. \quad (2.11)$$

The volume of free solvent in the resin phase, v, is a rather indefinite quantity, though $RT\ln K_H^M$ cannot be evaluated unless the value of v is determined. But, fortunately, when $RT\ln K_H^M$ is plotted against $1/D_s$ with constant v, the slope of the curve is unaffected by the value of v. Thus, it is possible to check the validity of Eq (2. 11). The measurements were carried out on the resin-alkali earth chloride systems in aqueous ethanol under the same conditions as stated in the preceding paper, except that one gram of the resin (dry weight) was added to the solution in each measurement. This procedure may assure us of the constancy of v, since the value of v is likely to be insensitive to the variation of alcohol concentration. But at the same time it follows that the mole ratio of the two species in the resin phase is no longer maintained at a constant value.

The plot of the data suggests in this case, too, the existence of the linear relationship between $RT\ln K_H^M$ and $1/D_s$ in the range of $D_s>55$. Moreover it is found that the relative value of $RT\ln K_H^M$ increases more rapidly for the heavier ion. By comparing the linear parts of the curves obtained for alkali and alkali earth ions, it is found that the order in the magnitude of the slope is $K^+>Na^+>\frac{1}{2}Ba^{++}>\frac{1}{2}Sr^{++}>\frac{1}{2}Ca^{++}Li^+>\frac{1}{2}Mg^{++}$, which comes into line with the sequence expected from Eq. (2. 11) and the values of n_H and n_M given by Stokes and Robinson.[2] These facts do not directly lead to the conclusion that the treatment given Section II is entirely adequate. Because of the complexities of the probem it is impossible at present to provide an exact quantitative expression of the phenomena associated with the solvent effects. The probem has been treated rather in a qualitative manner in Section II; a series of assumptions has been introduced either explicitly or implicitly, and several factors have been neglected for the sake of simplicity in the course of the computations. Therefore, Eq. (2. 8) or (2. 11) is to be regarded not as a theoretical formula but as a semi-empirical one. But it may be admitted that Eq. (2. 11) is a useful representation reflecting the general tendency of the solvent effects.

The Value of "v"

It was pointed out in the preceding report that the metal ion having the greater value

2) R. H. Stokes and R. A. Robinson, *J. Am. Chem. Soc.*, 70, 1870 (1948).

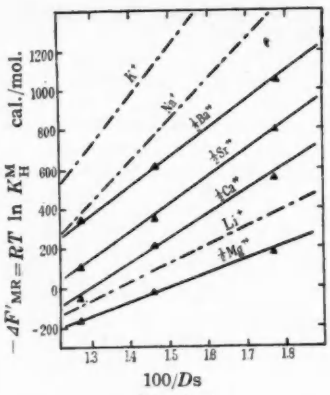

Fig. 2-2

of $RT\ln K_H^M$ in aqueous solution exhibits the more rapid increase of $RT\ln K_H^M$ with $1/D_s$. Consequently, in the graph of $RT\ln K_H^M$ plotted against $1/D_s$, the lines of barium, strontium and calcium ions should lie between those of sodium and lithium ions, and the line of magnesium ion should be found below that of lithium ion.

Since the first term of the right hand side of Eq. (2. 10) has been known from the experiment, the value of the second term must be determined so that the above requirements may be satisfied. By this procedure 0.20—0.25 ml. is found for the value of v per one gram of dry resin.

This result shows nothing but the fact that the ion behaves as if it were surrounded by this volume of free water in the resin phase. Besides, the value of v presumably depends upon the species of the ions in the resin and their quantities. But the found value seems to be not far from the real value of the free water in the resin.

Fig. 2-2 shows the results obtained by using this value for v.

Summary

The effect of the addition of non-electrolytes to the ion exchange system has been studied. It has been found that the dielectric constant of the solution gives a profound effect on the ion exchange equilibrium and that in the case of lower concentrations of alcohol a linear relationship exists between the apparent free energy change and the reciprocal of the dielectric constant. A working equation has been proposed to account for the relationships between the free energy change, dielectric constant, ionic species and valency of exchangeable ion.

The author would like to express his thanks to Professor Isamu Sano and Professor Kazuo Yamasaki for their interest and encouragement; also to Dr. Hidetake Kakihana for his helpful advice. He is much indebted to Mr. Yoshihiro Mori for experimental assistance. The cost of the research has been defrayed from the Scientific Research Grant of the Ministry of Education.

Chemical Institute, Faculty of Science, Nagoya University

Spectrochemical Study of Microscopic Crystals. VII.[1] *Absorption Spectra of Trans-dihalogeno-bis (ethylenediamine)-cobalt (III) Complexes*

By Shoichiro YAMADA, Akitsugu NAKAHARA, Yoichi SHIMURA and Ryutaro TSUCHIDA

(Received October 21, 1954)

In the former paper of this series[2] the present authors reported on the dichroism of the crystal of *trans*-dichloro-bis-(ethylenediamine) cobalt (III) salts. One of the conclusions therein, concerning the way of arrangement of the complex cations in the crystal of the hydrochloride dihydrate was found to be in disagreement with the result of X-ray investigation performed subsequently by one of the present authors.[3] The interpretation on the absorption bands of the praseo-salts in the previous paper was found to be in a dequate. We have, therefore, repeated the dichroism measurement of the hydrochloride and further measured the

1) Part VI, S. Yamada and R. Tsuchida, This Bulletin, 27, 436 (1954).
2) S. Yamada and R. Tsuchida, ibid., 25, 127 (1952).
3) A. Nakahara, Y. Saito and H. Kuroya, ibid., 25, 331 (1952).

dichroism with crystals of *trans*-dichloro-bis (ethylenediamine)-cobalt (III) perchlorate and the hydrobromide of *trans*-dibromo-bis (ethylenediamine)-cobalt (III) bromide. In this paper we present the results of the above measurements and discuss the results on the basis of the revised interpretation about the absorption bands.

Experimental

Materials.—Trans-dichloro-bis (ethylenediamine)-cobalt (III) perchlorate.—Green crystals were prepared according to the direction of Linhard et al.[4] These crystallize in rhombic plates belonging to the monoclinic system. The external form and dichroism are closely similar to those of *trans*-$[Co(en)_2Cl_2]$ $Cl\cdot HCl\cdot 2H_2O$.[2,3,5] In the dominant (001)-plane, the crystal exhibits a remarkable dichroism; it appears greenish yellow with the electric vector along the b-axis and blue with that perpendicular to the b-axis. Dichroism measurements were made along these two directions.

Trans-dibromo-bis (ethylenediamine)-cobalt (III) bromide hydrobromide dihydrate, $[Co(en)_2Br_2]Br\cdot HBr\cdot 2H_2O$.[6]—Green crystals were prepared by the method of Jörgensen.[7] This compound crystallizes in forms similar to those of the above praseo-salts, that is, in monoclinic crystals with well-developed (001)-planes. On the c-plane the crystal shows a striking dichroism; that is, it appears brownish yellow with the electric vector along the b-axis, and green with the electric vector perpendicular to the above. Dichroism measurements were made with respect to these directions.

Trans-dichloro-bis (ethylenediamine) cobalt (III) chloride hydrochloride dihydrate, $[Co(en)_2Cl_2]$ $Cl\cdot HCl\cdot 2H_2O$.—The preparation and properties were reported in the former paper.[2]

Measurements.—Quantitative dichroism measurements were performed with a microcrystal by Tsuchida-Kobayashi's microscopic method[8] in the region covering 2400 to 7500 Å. α denotes absorption coefficient per mm. of a crystal. Molecular absorption coefficients, K, were estimated from the relation, $K=10\,M\alpha/\rho$, where M and ρ represent the formula weight of the compound and the density of the crystal, respectively.

Results and Discussion

Dichroism of $[Co(en)_2Cl_2]$ $Cl\cdot HCl\cdot 2H_2O$ and $[Co(en)_2Cl_2]$ ClO_4.—Redetermined absorption spectra of a crystal of the hydrochloride, which differ slightly from those in the former paper,[2] are shown in Fig. 1, and data given in Table I. Results with the praseo-perchlorate are given in Fig. 2 and Table II.

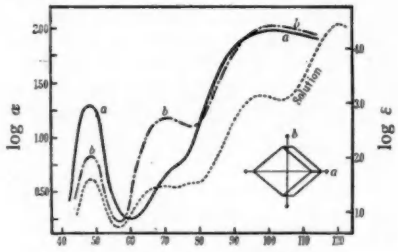

Fig. 1. Absorption spectra of $[Co(en)_2Cl_2]$ $Cl\cdot HCl\cdot 2H_2O$. The curve of the solution is taken from ref. 11.

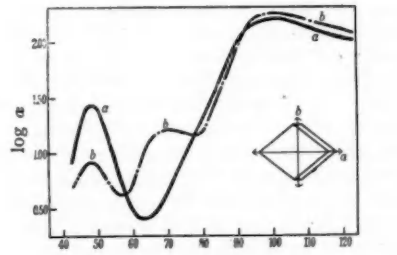

Fig. 2. Absorption spectra of $[Co(en)_2Cl_2]$ ClO_4.

TABLE I

ABSORPTION MAXIMA OF THE CRYSTALS OF $[Co(en)_2Cl_2]$ $Cl\cdot HCl\cdot 2H_2O$

	ν 10^{13}/sec.	log α	ν 10^{13}/sec.	log α	ν 10^{13}/sec.	log α
a-abs.	48.2	1.29	—	(0.65)	(100)	1.97
b-abs.	48.3	0.82	70	(1.18)	(102)	2.02

TABLE II

ABSORPTION MAXIMA OF THE CRYSTALS OF $[Co(en)_2Cl_2]ClO_4$

	ν 10^{13}/sec.	log α	ν 10^{13}/sec.	log α	ν 10^{13}/sec.	log α
a-abs.	48.0	1.44	—	(0.7)	(100)	2.20
b-abs.	48.1	0.91	70.8	(1.22)	(102)	2.25

In the former paper,[2] the authors presumed from the dichroism that the Cl-Co-Cl direction in the crystal of the hydrochloride should nearly conform with the b-axis.[9]

4) M. Linhard and G. Stirn, *Z. anorg. allg. Chem.*, 268, 105 (1952).

5) The notation, en, represents a molecule of ethylenediamine.

6) Two formulae have been proposed for this crystal, that is, one with two water molecules of crystallization and the other with one molecule of water. (Cf. "Gmelins Handb. anorg. Chem.", 8. Aufl., Teil 58 B, (1930) p. 252). In this paper we tentatively adopted the formula with two water molecules of crystallization, since the crystal shows a close similarity to that of $[Co(en)_2Cl_2]Cl\cdot HCl\cdot 2H_2O$.

7) S. M. Jörgensen, *J. prakt. Chem.*, (2) 41, 444 (1890).

8) R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds, (in Japanese)" Zoshindo, Osaka, Japan, (1944), p. 180. See also the previous papers of this series.

9) The a, b and c-axes adopted in the present paper and former paper (Ref. 2) correspond, respectively, to the c-, b- and a-axes in (Ref. 3).

This conclusion, however, was found to be incorrect. According to the X-ray crystal analysis with $[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$,[3] the Cl-Co-Cl direction in this crystal nearly conforms with the a-axis,[9] more exactly, inclined by about 18° to the a-axis, and by 76° to the b-axis. Using the data of the X-ray analysis, the components of the molecular absorption coefficients for the praseo-complex cation in the crystal of the hydrochloride dihydrate were calculated from the data in Table I, and shown in Table III.[10] As can be seen in Table III, the absorption band at 48×10^{13}/sec. is polarized in the Cl-Co-Cl direction, and the absorption band at 70×10^{13}/sec. is polarized in the plane formed by a cobalt and four nitrogen atoms. $K_{Cl\text{-}Co\text{-}Cl}/K_{Co\text{-}en}$ is found to be 5.9 for the former band and 1/5.5 for the latter band.

Table III

Dichroism of the complex-ion, *trans*-$[Co(en)_2Cl_2]^+$

	ν, 10^{13}/sec.	K_a	K_b	$K_{Cl\text{-}Co\text{-}Cl}$	$K_{Co\text{-}en}$
Band Ia	48	431×10^3	136×10^3	470×10^3	80×10^3
Band Ib	71	98.8×10^3	346×10^3	68×10^3	375×10^3

Table IV

Absorption maxima of the crystals of $[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$

	ν	$\log\alpha$	ν	$\log\alpha$	ν	$\log\alpha$	ν	$\log\alpha$
a-abs.	44.6	1.47	——	——	77	2.18	98.5	2.22
b-abs.	45.0	0.77	65	1.16	87	2.13	103	2.27
		$\log\varepsilon$		$\log\varepsilon$		$\log\varepsilon$		$\log\varepsilon$
solution[a]	45.6	1.73	65.0	1.49	84.3	3.35	103.8	4.34

a) These values are taken from ef. r12.

Linhard et al.[11] extensively studied absorption spectra of *trans*-dihalogeno-tetrammine- and bis (ethylenediamine)-cobalt (III) complexes in solution, and showed from comparison of absorption spectra of many complexes that in the dihalogeno-complexes the "first band,"[12] which usually appears with one band maximum, splitts itself into two bands. Thus the bands at 48 and 70×10^{13}/sec. of the praseo-salts correspond to the first band. The band at 100×10^{13}/sec. may be considered as the "specific band."[13] Its second band may be covered under the large specific band.

The present measurement shows that the praseo-perchlorate in the crystalline state displays absorption bands at 48, 71 and 100×10^{13}/sec., which correspond with those of the hydrochloride. Corresponding bands are also observed in the absorption spectra of the solution.

It is also found that the crystal of the perchlorate shows a quite similar dichroism to that of the hydrochloride. Comparison of the dichroism and absorption spectra of both the crystals indicates that in the crystal of the perchlorate, just as in the case of the crystal of the chloride, the Cl-Co-Cl direction in the complex cation is nearly coincident with the a-axis. The angle which the Cl-Co-Cl direction makes with the a-axis in this crystal is estimated to be even a little smaller than in the crystal of the hydrochloride dihydrate.

The band at 102×10^{13}/sec., which may be assigned to the "specific band,"[13] mainly due to the chlorine atoms in coordination, seems to be only slightly polarized. For this band, the Cl-Co-Cl absorption is found to be slightly bathochromic to the Co-en absorption.[14] It seems interesting enough that the hydrochloride and perchlorate crystallize in a closely similar form, in monoclinic plates with almost equal angles in the well-developed (001)-plane, showing also a quite similar dichroism, in spite of great difference in the size of the anions.

Dichroism of the $[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$. —Results are shown in Fig. 3 and given in Table IV. The crystal shows absorption bands at 45, 65, 86 and 103×10^{13}/sec. These bands find corresponding bands in the absorption spectra of the solution at almost identical wave-lengths, although the intensity relation among bands is not same as that

10) Some of the values in Ref. 2 were corrected after repeated measurements. $K_{Cl\text{-}Co\text{-}Cl}$ and $K_{Co\text{-}en}$ are molecular absorption coefficients with the electric vector along the Cl-Co-Cl direction and along the plane constructed from one cobalt and four nitrogen atoms, respectively.

11) M. Linhard and M. Weigel, *Z. anorg. allg. Chem.*, 271, 101 (1952).

12) R. Tsuchida, This Bulletin, 13, 388, 436 (1938).

13) R. Tsuchida, and M. Kobayashi, ibid., 13, 471 (1938).

14) The X-Co-X-absorption, X being halogens, represents the absorption with the electric vector along the X-Co-X direction, and the Co-en-absorption the absorption with the electric vector along the plane formed by one cobalt and four nitrogen atoms.

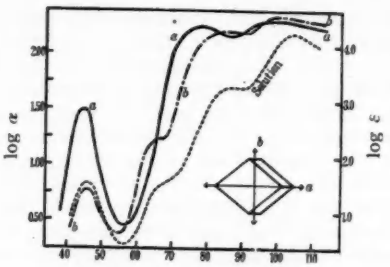

Fig. 3. Absorption spectra of $[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$. The curve of the solution is taken from ref. 11.

for the solution. The first band of this compound, as in the case of the corresponding dichloro-compound, may be considered to split into two band maxima. Thus the bands at 45 and 65×10^{13}/sec. of $[Co(en)_2Br_2]^+$ correspond to the bands at 48 and 70×10^{13}/sec. of $[Co(en)_2Cl_2]^+$. It is readily seen that the cations, $[Co(en)_2Br_2]^+$ and $[Co(en)_2Cl_2]^+$, show quite similar dichroism. It may be supposed that the band at 45×10^{13}/sec. is almost completely polarized in the Br-Co-Br direction and that the band at 65×10^{13}/sec. is polarized in the plane formed by one cobalt and four nitrogen atoms. It is seen that the difference in the absorption coefficient for the band at 45×10^{13}/sec. between the b- and a- absorptions is even larger than that for the corresponding band with the hydrochloride of the praseo-salt. It is, therefore, most probable that the Br-Co-Br direction of the complex cations in the crystal corresponds almost exactly with the a-axis.

For the band at $70—90 \times 10^{13}$/sec., which may tentatively be assigned to the "specific band,"[13] mainly due to the bromine atoms in co-ordination, the Br-Co-Br-absorption[14] is bathochromic to the Co-en absorption. This relation agrees with that induced for the specific band of other ligands.[15] For the band at about 100×10^{13}/sec., which is assumed to be the "third band,"[12] the Br-Co-Br-absorption is slightly bathochromic to the Co-en-absorption. The relation is also found to be in good agreement with that for the corresponding band of $[Co(en)_2Cl_2]^+$.

Further, it is to be noted that $[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$ appears to be isomorphous with $[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$, both crystallizing in a closely similar form, monoclinic plates with nearly equal angles. Thus it is probable that in the crystals of the above two compounds the complex cations take an isomorphous arrangement, and, in consequence, that in the crystal of the latter compounds, like in the former,[15] there might exist a network of hydrogen bonds involving bromine atoms. This being the case, the compound would afford one of the few examples that would involve bromine atoms forming hydrogen bonds. The crystal structure investigation of the compound is expected to yield interesting results.

Absorption Spectra of *Trans*-dihalogeno-bis(ethylenediamine)-compounds in the Crystalline State.—As stated in the above paragraph, Linhard et al. showed clearly that in the solution of *trans*-dihalogeno-complexes the first band, which in most complexes appears with one band maximum, shows two separate maxima. Thus the bands at 48 and 70×10^{13}/sec. for $[Co(en)_2Cl_2]ClO_4$ and the bands at 45 and 65×10^{13}/sec. for $[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$ are considered to correspond to the first band. For the first band of the *trans*-dihalogeno-complexes, the following relation can be induced. *The trans-dihalogeno-complexes show two separate absorption maxima corresponding to the first band. The absorption at the longer wave-length, polarized in the X-Co-X direction, takes place with the electric vector along the X-Co-X direction, and the absorption at the shorter wave-length occurs with the electric vector along the plane constructed from one cobalt and four nitrogen atoms.* The fact that the transition along the direction binding cobalt and halogen atoms requires much less energy much less than the transition in the plane formed by one cobalt and four nitrogen atoms may be understood qualitatively from the semi-empirical relation that halogen stands far behind ethylenediamine in the spectrochemical series;[12] the linkage between a metal and a nitrogen atom of an amine in a complex causes an electronic absorption in the shorter wave-length regions than the linkage between the metal and a halogen atom. Such a clear splitting of the first band as was observed in the above instances has not been found in many other complexes of a *trans*-configuration.[17] It may be assumed that, when two ligands in *trans*-positions stand much lower or higher in the spectrochemical series than the other four ligands, the complex would have its first band definitely split into two bands. In every *trans*-

15) To be submitted later.

16) In Ref. 3. on the crsytal structure of $[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$, only the word "N-Cl bond" was used, and not any word, "hydrogen bond between N and Cl." But since the distance between N and Cl atoms is so short, 2.9 Å, that the bond is surely expected, it is reasonable to suppose that the H- atom originally attached to N of the ethylenediamine molecule should be directed toward Cl, and that the bond between the N and Cl should be a kind of hydrogen bonds.

17) To be submitted later.

disubstituted-tetrammine complex, more or less marked splitting of its first absorption band might be expected from symmetry consideration. But when the ligands in *trans*-positions stand rather close to en or NH_3 in the spectrochemical series, the splitting may be less distinct. Besides, the electrostatic effect of ligand ions could not be overlooked. Thus the strongly ionic character of the linkage between cobalt and chlorine atoms might be another cause for the above splitting of the band.

For both the third band and the specific band, the X-Co-X absorption is found to be slightly bathochromic to the Co-en-absorption. The relation that for the above two bands the electronic transition along the X-Co-X direction requires less energy than that along the Co-en plane may readily be understood qualitatively on the basis of the idea about the origins of the absorption bands,[12,13] proposed by one of the present authors, that the third absorption band is due to charge transfer between the central ion and a ligand anion which is especially facilitated in the case of the existence of two anions in *trans*-positions, and that the specific band is due to the ligand concerned in co-ordination.

Absorption Spectra of the *Trans*-dihalogeno-tetrammine-complexes in Solution.— Absorption spectra of the praseo-salts in solution may be understood in the light of the dichroism. Earlier, Mathieu[18] and one of the present authors[19] pointed out the possibility that absorption bands of sexa-co-ordinated complexes having lower symmetry might consist of a set of component absorptions, which would appear as separate maxima in some cases. Later, Ilse et al.[20] treated the absorption spectra of octahedral complexes of titanium (III) in terms of the group theory, and showed that the hexa-co-ordinated complexes of tetragonal symmetry involve more energy levels, and therefore give rise to more electronic transitions than those of octahedral symmetry. Linhard et al. showed experimentally that the *trans*-dihalogeno-complexes should have their first absorption bands split into two components and ascribed this phenomenon to the tetragonal symmetry of the complex-cations. The present dichroism measurements seem to afford an evidence for the above idea that the praseo-salts should exhibit two separate maxima corresponding to the components of their first band. Thus, of the two maxima for the first band, the one at the longer wave-length has been shown to be due principally to the transition along the Cl-Co-Cl direction, and the other at the shorter wave-length may be due to the transition along the plane formed by one cobalt and four nitrogen atoms. A small inflation at 75×10^{13}/sec. in the absorption spectrum of the solution of the dichloro-bis(ethylenediamine)-cobalt (III)-compound may be considered as due to the second absorption band.

Similar explanation may be applied to the absorption spectrum of the solution of dichloro-tetrammine-cobalt (III)-ion. Since the complex cation, *trans*-$[Co(NH_3)_4Cl_2]$, is unstable in solution, the conventional method is not applicable in determining the absorption spectrum of the complex. By making spectrographic analysis of the aquotization reaction, one of the present authors[21] determined the absorption spectrum of this complex cation (Table V). As in the case of the corresponding ethylenediaminecompounds, it seems reasonable to suppose that the maxima at 48 and 62×10^{13}/sec. correspond to the first band. Thus the band at 48×10^{13}/sec. may be due to the transition along the Cl-Co-Cl direction, and the one at 62×10^{13}/sec. may be due to the transition along the plane formed by one cobalt and four nitrogen atoms. The slight inflation at 75×10^{13}/sec. may be assigned as the second absorption band. The bands at 100 and 120×10^{13}/sec. should be assigned to the specific band and the third band, respectively.

On the basis of the foregoing discussion,

18) J. P. Mathieu, *Bull. soc. chim. France*, [5], **3**, 463 (1936).
19) R. Tsuchida, *J. Chem. Soc. Japan*, **59**, 586 (1938).
20) F. E. Ilse and H. Hartmann, *Z. physik. Chem.*, **197**, 239 (1951).
21) R. Tsuchida, This Bulletin, **11**, 721 (1936).

TABLE V

ABSORPTION MAXIMA OF *trans*-DIHALOGENO-COBALT (III) COMPLEXES IN SOLUTION

		1st Band				2nd Band		Specif. Band		3rd Band	
		ν	$\log\varepsilon$	ν	$\log\varepsilon$	ν	$\log\varepsilon$	ν	$\log\varepsilon$	ν	$\log\varepsilon$
$[Co(NH_3)_4Cl_2]Cl$	(a)	50	1.21	62.3	1.41	77.0	1.40	100	3.16		
	(b)	47.7	1.63	63.0	1.38	74.8	1.54	98.9	2.86	118.4	4.39
$[Co(en)_2Cl_2]Cl$	(b)	48.4	1.61	67.5	1.46	77.8	1.49	97.5	3.12	120.8	4.43
	(c)	48.0	1.54	66.7	1.41	78.9	1.64	—	—	119.0	4.31
$[CO(en)_2Br_2]Br$	(b)	45.6	1.73	65.1	1.49	—	—	84.3	3.35	103.8	4.34

(a) ref. 22. (b) ref. 11. (c) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).

the absorption bands of the above *trans*-dihalogeno-complexes in solution may be designated as given in Table V.

The dichroism measurements should be expected to throw light upon the origins of the absorption bands of metallic complexes. Unfortunately, the second band has not been found as a separate maximum in the three compounds investigated. The investigation of the data obtained by Linhard et al.[11] indicates that the second band of the *trans*-dihalogeno-complexes appears to show no splitting, at least, none so distinct as the first band. On the other hand, the above measurements have shown that the first band splits itself into two bands. It seems, therefore, evident that the two bands, the first and second bands, should be ascribed to two transitions of different electrons. Although the decisive discussion on the origins of the first and second bands must be postponed until other materials are accumulated, the idea that the first band originates from *d*-electrons of a cobalt atom and the second band from co-ordination electrons seems to be one of the most probable.

Summary

Dichroism of the crystals of *trans*-$[Co(en)_2Cl_2]ClO_4$, $[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ and $[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$ have been quantitatively determined by Tsuchida-Kobayashi's microscopic method in the visible and ultraviolet regions.

As to the dichroism of the *trans*-dihalogeno-complexes, the following relations have been induced. The first band splits itself into two component absorptions. One at the longer wave-length is polarized in the X-Co-X direction, and the other at the shorter wave-length is polarized in the Co-en plane. For the third and specific bands, the X-Co-X-absorption is bathochromic to the Co-en-absorption.

On the basis of the above results, absorption spectra of several praseo-complexes in solution have been discussed.

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Conductivity of Aqueous Potassium Dodecyl Sulfonate at Various Temperatures and with Solubilized Benzene

By Wei-chuwan Lin

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Introduction

The somewhat abrupt change with concentration of many physical properties of solution of long-chain electrolytes has been attributed to the formation of micelles, and the concentration at which this change occurs has been termed " the critical concentration for the formation of micelles ".[1]

Electrical conductivity is one of the properties which may be utilized for the determination of the critical concentration. It has been pointed out[2,3], that if the specific conductivity be plotted against the concentration the critical concentration is given by the intersection of the resulting two straight lines.

We have determined the specific conductivity of aqueous solutions of potassium dodecyl sulfonate as a function of the concentration of the salt at temperatures ranging from 25 to 60°C and in the presence of varying amounts of solubilized benzene.

In this manner we have determined the critical concentration of potassium dodecyl sulfonate at several different temperatures and at several different concentrations of solubilized benzene. We also could obtain data for the effect of solubilized benzene on the relation between equivalent conductivity and concentration at constant temperature.

Experimental

Potassium dodecyl sulfonate was prepared by the reaction between dodecyl bromide and aqueous potassium sulfite. The salt was washed sev-

1) See references quoted by M. L. Corrin, H. B. Klevens, and W. D. Harkins, *J. Chem. Phys.*, **14**, 480 (1946).
2) K. A. Wright, A. D. Abbott, V. Sivertz and H. V. Tartar, *J. Am. Chem. Soc.*, **61**, 549 (1939).
3) A. P. Brady and H. Huff, *J. Colloid Sci.*, **3**, 511 (1948).

eral times with petroleum ether, recrystallized twice from ethanol and twice from conductivity water and dried in vacuo. Benzene was of reagent grade and used without further purification.

Solutions containing solubilized benzene were prepared by adding weighed amounts of the salt to solutions of benzene in water. These solutions were made up by weight-volume.

Conductivity measurements were made in a Leeds-Northrup pyrex conductivity cell at 1000 cycles. A Leeds-Northrup Jones bridge and electronic amplifier and oscillator were used and the null points determined on an oscilloscope. An oil bath constant to 0.01°C was used for temperature control; cell constants were determined for each temperature. The electrodes were platinized.

Critical concentrations were determined graphically as the point of intersection of two straight lines in the plot of specific conductivity against concentration.

Results and Discussion

Plots of specific conductivity versus concentration at temperatures five degrees apart in the range of 25 to 60°C are given in Fig. 1. These are characteristic of solutions

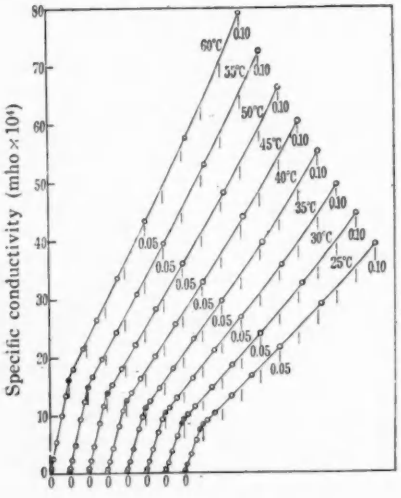

Fig. 1. Specific conductivity plotted against volume normality for aqueous solution of potassium dodecyl sulfonate

of long-chain electrolytes. Similar plots of the equivalent conductivity as a function of the square root of the concentration are given in Fig. 2. The form of these curves has been discussed by Wright, Abbott, Sivertz and Tartar[2], by Wright and Tartar[4], and by

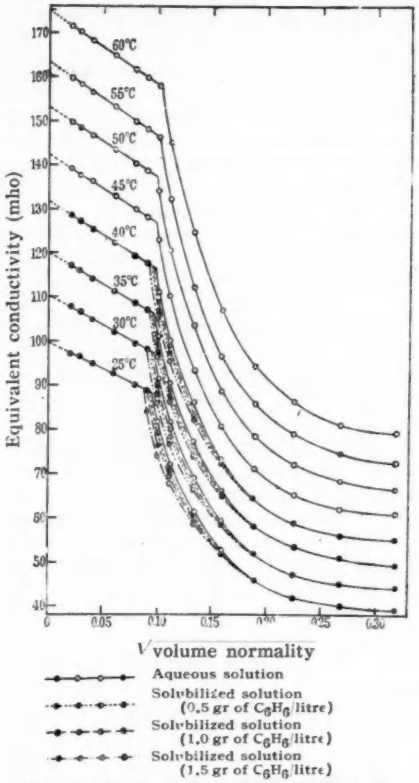

Fig. 2. Equivalent conductivity plotted as a function of the square root of potassium dodecyl sulfonate concentration in the presence of varying amounts of solubilized benzene

Ralston and Hoerr[5]. The rapid increase in equivalent conductivity at the higher salt concentrations has been attributed to "retrograde dissociation".

Plots of the specific conductivity versus salt concentration at several temperatures in the presence of varying amounts of solubilized benzene are given in Fig. 3. Similar plots of the equivalent conductivity as a function of the square root of the salt concentration at several temperatures in the presence of varying amounts of solubilized benzene are also given in Fig. 2. It is evident that (a) the solubilized benzene does not affect the conductivity at concentrations below the critical concentration, (In this range the salt is supposedly completely ionized and the Debye-Hückel-Onsager limiting law may be applied.), (b) the critical concentration is lowered by

4) K. A. Wright and H. V. Tartar, *J. Am. Chem. Soc.*, **61**, 544 (1939).

5) A. W. Ralston and C. W. Hoerr, *J. Am. Chem. Soc.*, **64**, 772 (1942).

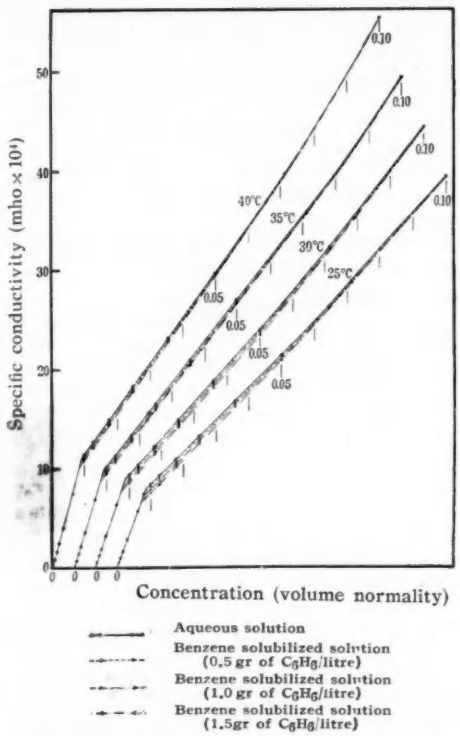

Fig. 3. Specific conductivity plotted against concentration of potassium dodecyl sulfonate in the presence of varying amounts of solubilized benzene

the solubilized benzene with the amount of lowering increasing with the increase of benzene concentration, and (c) the effect of added benzene becomes increasingly less as the salt concentration becomes greater.

Change of Critical Concentration with Temperature.—The variation in critical concentration with temperature has been discussed by several authors. Tartar and his coworkers have reported that with long-chain sulfonates in the range of 40 to 80°C the critical concentration increases with temperature[2]. Brady and Huff[3] found a decrease with temperature for lauryl sulfonic acid and potassium laurate in the range of 0 to 90°C. A similar decrease was noted by Scott and Tartar[5] for quaternary ammonium salts between 25 and 60°C. The above estimates were made from conductivity data. Using the dye method Herzfeld observed a minimum in the critical concentration as the temperature was varied from 0 to 80°C[7]. The results obtained in this study as shown in Table I and Fig. 4 are in agreement with

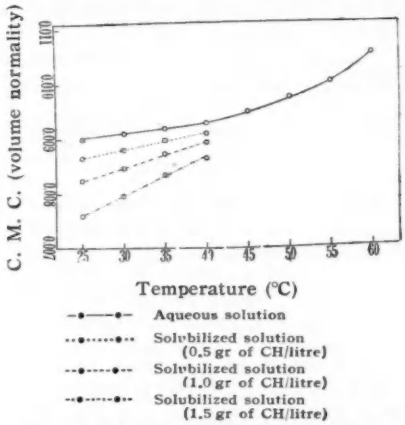
C. M. C. (volume normality)
Temperature (°C)
Aqueous solution
Solubilized solution (0.5 gr of CH/litre)
Solubilized solution (1.0 gr of CH/litre)
Solubilized solution (1.5 gr of CH/litre)

Fig. 4. Change of C. M. C. with temperature

those noted for the sulfonates by Tartar et al[2,6]; namely, that the critical concentration increases with temperature.

TABLE I

CHANGES OF C. M. C. FOR AQUEOUS SOLUTIONS OF POTASSIUM DODECYL SULFONATE WITH CHANGE IN TEMPERATURE AND CONCENTRATION OF SOLUBILIZED BENZENE

Temperature (°C)	Amount of benzene solubilized (grams of C_6H_6/litre of aqueous solution)			
	0	0.5	1.0	1.5
25	0.0090^0	0.0086^5	0.0082^5	0.0076^0
30	0.0091^0	0.0088^0	0.0084^5	0.0079^5
35	0.0092^0	0.0090^0	0.0087^5	0.0083^5
40	0.0093^0	0.0091^0	0.0089^0	0.0086^5
45	0.0095^0	—	—	—
50	0.0097^5	—	—	—
55	0.0100^0	—	—	—
60	0.0104^0	—	—	—

The Effect of Benzene on the Critical Concentration.—The effects of various concentrations of solubilized benzene on the critical concentration of potassium dodecyl sulfonate are given in Table I and plotted in Fig. 5. At constant temperature the lowering of the critical concentration increases with the increase of benzene concentration. The lowering becomes less marked with increasing temperature.

These results are in essential agreement with those obtained by Lingafelter, Wheeler

6) A. B. Scott and H. V. Tartar, *J. Am. Chem. Soc.*, 65, 692 (1943).

7) S. H. Herzfeld, Unpublished work

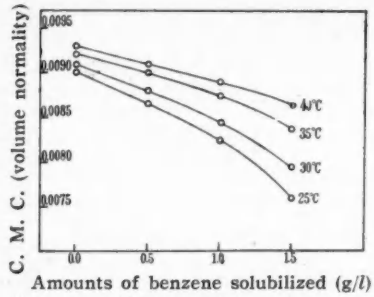

Fig. 5. C. M. C. plotted against amount of solubilized benzene

and Tartar[8] for benzene and several sodium alkylsulfonates by an interfacial tension method.

An interpretation of this work must rest upon the analysis of the various energy terms involved in micellization. Herzfeld, Corrin and Harkins[9] have suggested two such energy terms of major importance. First a decrease in free energy is brought about by removal of the long-chain ion from its aqueous environment into the interior of the micelle (environmental term). This term will be maximal when the removal of the non-polar chain from the water is as complete as possible. Second, short range repulsive terms come into play as the polar head groups are brought together in the micelle and this repulsive energy term must be taken into account. On the basis of this analysis the micelle would contain fewer ions than the limit set by steric factors.

In the presence of relatively non-polar additives such as benzene it might be expected that the environmental terms might be increased in magnitude and that the repulsive term might be decreased by the inclusion of benzene in the micelle. This would lead to (a) a decrease in critical concentration and (b) a change in the size or the number of long-chain ions per micelle or both. It would seem from the conductivity measurements reported here that the change in micelle size in the presence of benzene cannot be very great since at concentrations exceeding the critical concentration there is little difference between the conductivity terms in the presence and absence of benzene. It is possible, although unlikely, that a change in micelle size is exactly balanced by a change in micelle ionization.

We do not propose to discuss the conductivity curves completely at this time.

8) F. C. Lingafelter, O. L. Wheeler and H. V. Tartar, *J. Am. Chem. Soc.*, **68**, 1490 (1946).
9) S. H. Herzfeld, M. L. Corrin and W. D. Harkins, *J. Phys. & Colloid Chem.*, **54**, 271 (1950).

Summary

The specific conductivity of aqueous solutions of potassium dodecyl sulfonate has been measured as a function of concentration in the presence and absence of solubilized benzene in the temperature range between 25 and 60°C.

Below the critical concentration for the formation of micelles solubilized benzene has no effect on the conductivity. In the critical concentration range there is a marked effect which decreases with salt concentration and finally becomes negligible.

The critical concentration decreases in the presence of solubilized benzene; this effect becomes more marked as the benzene concentration is increased. The critical concentration increases with increasing temperature both in the presence and absence of benzene.

The experimental part of this work was done at George Herbert Jones Laboratory, University of Chicago, Ill., U. S. A. The author would like to express his hearty gratitude to Dr. M. L. Corrin for many fruitful discussions during his stay at the University of Chicago, and for personal communications after his return to Formosa.

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SHORT COMMUNICATIONS

A Reaction of Malonic Ester with Vinyl Acetate

By Teiji TSURUTA

(Received February 7, 1955)

Diethyl sodio malonate has been found to react readily with vinyl acetate to give ethylidenedimalonic ester.

To a solution of 4 g. (1/6 atom) of metallic sodium and 80 g. (1/2 mol.) of diethyl malonate in 200 ml. of absolute ethanol, was added 44 g. (1/2 mol.) of vinyl acetate. The temperature was maintained at 20°. After the mixture was stirred for one hour, it was acidified with 15 ml. of glacial acetic acid and the solvent removed under reduced pressure. The residual liquid was taken up in ether, washed with water, and dried over anhydrous sodium sulfate; the solvent was removed and the residue distilled under reduced pressure. There was obtained 48 g. of a viscous oil, b.p. 165–171° (9 mm), which was hydrolysed with barium hydroxide. The resulting barium salt was dissolved in hydrochloric acid and filtered through a column of Amberlite IR-120 (SO_3H-type). From the filtrate, on removing solvent in vacuo, there was obtained crystalline powder (I), m.p. 155° (with decomposition). By decarboxylation at 160°, (I) was converted to crystals (II) of m.p. 85°. The crystals (I) and (II) were proved to be ethylidenedimalonic acid and β-methylglutaric acid by mixed melting with authentic specimens.

Since active hydrogen compounds were reported to react with vinyl acetate to give vinyl-, vinylidene- or ethylidene-derivatives in the presence of a mercuric salt[1], the mechanism of the present condensation reaction of sodio malonic ester with the vinyl ester is to be considered in connection with *the vinyl exchange reaction*.

Full details will be reported later.

The author is grateful to Professor R. Oda and Professor J. Furukawa for advice, and to Miss Kihara for assistance.

1) R. L. Adelman, U.S.P., 2,550, 439 (1951); *Chem. Abstr.* **45**, 8035 (1951); *J. Am. Chem. Soc.*, **75**, 2678 (1953).

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On the Role of a Cytochrome in the Thiosulfate Reduction by Sulfate-Reducing Bacterium

By Makoto ISHIMOTO and Jiro KOYAMA

(Received January 22, 1955)

In a previous report (1) we have shown that a cell-free extract which was obtained from ground cells of sulfate-reducing bacterium displaved a marked activity of reducing thiosulfate to hydrogen sulfide in the presence of molecular hydrogen. From the extract we could separate hydrogenase and thiosulfate reductase (2) both of which are conceivably involved in the process in question. The mixture of these separated enzymes, however, were found to be totally inactive in cataysing the said reaction. A marked enhancement of the reaction rate was observed when methyl viologen was added to the enzyme mixture, indicating that the dye-stuff acted as an intermediary carrier filling the missing link between the enzyme systems. The course of events occurring in this case was supposed to be as follows:

$$H_2\cdots\underset{\text{genase}}{\text{Hydro-}}\cdots\underset{\text{carrier}}{\text{Intermediary}}\cdots\underset{\text{reductase}}{\text{Thiosulfate}}\cdots S_2O_3^{--}$$
(Methyl viologen)

Recently we found (3), in confirmation of the report by Postgate (4), that a certain cytochrome (showing absorption maxima at 419 mμ and 553 mμ in reduced state, and at 410 mμ in oxidized state) is contained in the cells of sulfate-reducing bacterium. The present paper deals with the isolation of this cytochrome from bacterial cells and the elucidation of its role as an intermediary carrier, similar to that assigned to methyl viologen in the above scheme, in the mechanism of thiosulfate reduction.

The procedure of isolation of the cytochrome was similar to that for cytochrome *c* (5). Acetone-dried cells of the bacterium were extracted with M/15 phosphate buffer of pH 6.4. On adding acetone to the extract in concentration of 33–66%, there appeared a precipitate which was dissolved in M/150 phosphate buffer of pH 7.0, dialyzed against the same buffer overnight and then passed through the column of ammonium salt of cation-exchange resin, Amberlite IRC-50. While the cytochrome was absor bed on the top

of the column, thiosulfate reductase, hydrogenase and a green pigment (3) as well as the greater part of porteins ran through it without being adsorbed. By elution with a mixture of ammonium chloride and hydroxide, the cytochrome absorbed could be separated in two fractions. Absorption spectra of these two fractions were hardly distinguishable from each other, both showing a maximum at 410 mμ, the Soret band of oxidized form. Compared with the strong absorption at 410 mμ, there was only insignificant absorption at 280 mμ, indicating that the solution of cytochrome contained, if any, only a small amount of proteinous impurities.

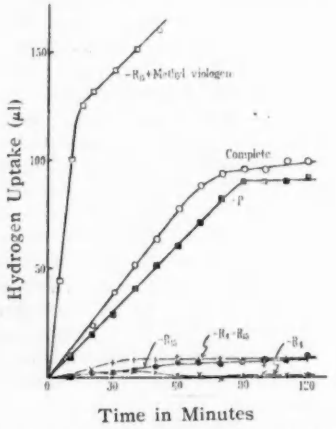

Fig. 1. Reaction between H_2 and thiosulfate (measured by H_2-uptake) caused by reconstructed system of various combinations.

H_2-uptake was measured with Warburg's manometer. Volume of each reaction mixture: 2.25 ml.; temperature: 30° C.; atmosphere: H_2. The center well contained 0.2 ml. of alkali.

The "complete" system was composed of:

(i) 0.5 ml. of suspension of particulate hydrogenase preparation (P) (800 hydrogenase units (2)),

(ii) 0.4 ml. of crude thiosulfate reductase preparation (R4) which was almost free from the cytochrome (70 reductase units (2)),

(iii) 0.75 ml. of the cytochrome preparation (R15) (0.55 cytochrome units (2)),

(iv) 0.2 ml. of 0.2 M phosphate buffer of pH 7.0, containing 6 mg. of egg albumin and 5 μM of $Na_2S_2O_3$.

No hydrogen uptake occurred in the absence of thiosulfate.

The non-absorbed solution containing thiosulfate reductase and hydrogenase showed no activity of reducing thiosulfate in the presence of hydrogen. The same was true when the solution was supplied with an additional quantity of hydrogenase.* A striking increase in the activity of the mixture was observed when the second fraction of the cytochrome was added to the mixture of non-adsorbed solution and hydrogenase preparation. (Fig. 1). Of interest is to note that the first fraction of cytochrome was quite ineffective in accelerating the reaction rate. The effectiveness (as well as the absorption spectrum) of the cytochrome in the second fraction was not modified by boiling the fraction for 3 minutes. This fact the accelerating effect of the fraction is not due to some thermolabile proteinous substances which might have been admixed with the cytochrome in the fraction.

The evidence presented here makes it quite plausible to assumed that the cytochrome obtained in the second fraction is an intermediary carrier, intrinsic to bacterial cells, which functions as a link between the systems of thiosulfate reductase and hydrogenase, just as did methyl viologen in the experiment reported previously. It should be added that the cytochrome in question could not be substituted in its carrier-function by cytochrome *c* from bovine heart muscle (6) or diphosphopyridine nucleotide.

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* Although the original non-adsorbed solution contained a certained amount of hydrogenase, its activity was found to be comparatively less than that of co-existing thiosulfate reductase. The preparation of hydrogenase added was the centrifugate (at 16000×g) from the extract which was obtained from finely ground barterial cells.

1) M. Ishimoto, J. Koyama, Y. Nagai, *J. Biochem. Japan.* **42**, 41 (1955).
2) M. Ishimoto, J. Koyama, Symposium on Enzyme Chemistry, **10**, 77 (1954).
3) M. Ishimoto, J. Koyama, Y. Nagai, *J. Biochem. Japan*, **41**, 763 (1954).
4) J. Postgate, *Biochem. J.*, **56**, xi (1954).
5) E. Margoliash, *Biochem. J.*, **56**, 535 (1954).
6) D. Keilin, E. F. Hartree, Proc. Roy. Soc. London, **B122**, 289 (1937).

Determination of thorium by Organic bases

By G. S. DESHMUKH and J. XAVIER

(Received December 13, 1954)

Jefferson[1] and Hartwell[2] reported the use of various amines and organic bases for the quantitative estimation of thorium in presence of rare earths. Further work by Atanasiu[3] and Schiotz[4] and Ismail and Hartwood[5] showed that pyridine, quinoline and hexamine are effective for the separation of thorium from cerium earths. An investigation along these lines seemed to promise well because it was considered that among the numerous hitherto uninvestigated organic bases, suitable precipitants might be found for the quantitative determination of thorium and its separation from rare earths and other familar congeners. Series of trial experiments were therefore carried out using *o*-tolidine, dianisidine, *p*-phenylenediamine, *o*-anisidine and *o*-phenetidine as precipitants for thorium. The present communication reports results obtained with the above bases and shows that *o*-anisidine and *o*-phenetidine afford a quantitative separation of thorium from trivalent rare earths.

Experimental

The organic bases used as precipitants were of Merck's reagent grade quality and were purified by repeated recrystallisation or/and distillation. An aqueous thorium chloride (or nitrate) solution was prepared and its thorium content was determined by *m*-nitrobenzoic[6] and sebacic acids.[7] In the case of *o*-tolidine, dianisidine and *p*-phenylenediamine the following procedure was adopted for precipitating the corresponding thorium complex.

To an aliquot quantity (10 ml.) of the thorium solution about 20–30 ml. of alcohol was added and the solution was heated to 90°C. A saturated alcoholic solution of the base was now run in a thin stream with constant stirring till the precipitation was complete, followed by about 5–10 ml. of alcohol. The contents were boiled for a couple of minutes. The precipitate was allowed to settle for an hour, filtered through Whatman 40, washed with cold alcohol, dried and ignited to ThO_2. For obtaining reproducible and accurate results, it is necessary to add the precipitant to an almost boiling hot solution of thorium salt containing an equivalent volume of alcohol and also to continue boiling at least for a few minutes after the complete precipitation of the thorium complex.

A representative group of results is given in Table I.

Since cerium and other trivalent rare earths are also precipitated by the above organic bases under the above experimental conditions, whose adaptability in quantitative analysis is restricted only to the determination of thorium in its aqueous solution.

Series of experiments carried out with *o*-phenetidine and *o*-anisidine, however, showed that these ammines could be used for the precipitation of thorium and its separation from trivalent rare earths e. g. Ce, La, Y and Er.

To a known volume of the thorium solution mixed with varying quantities of the above trivalent salt solutions and an equal portion of alcohol, an alcoholic solution of *o*-phenetidine or *o*-anisidine was added. The

TABLE I

Expt No.	Wt. of ThO_2 (g.) *m*-nitrobenzoic acid (a)	Wt. of ThO_2 (g.) *o*-tolidine (b)	dianisidine (c)	*p*-phenylenediamine (d)	Difference a~b	a~c	a~d
1	0.0640	0.0640	0.0638	0.0641	. .	0.0002	0.0001
2	0.0922	0.0919	0.0923	0.0923	0.0003	0.0001	0.0001
3	0.1152	0.1148	0.1149	0.1153	0.0004	0.0003	0.0001
4	0.1164	0.1164	0.1165	0.1165	. .	0.0001	0.0001
5	0.1378	0.1379	0.1376	0.1378	0.0001	0.0002	. .
6	0.1390	0.1392	0.1388	0.1390	0.0002	0.0002	. .

1) A.M. Jefferson, *J. Amer. Chem. Soc.*, 24, 540 (1902).
2) B.L. Hartwell, ibid. 25, 1128 (1903).
3) I.A. Atanasiu, *Ber.*, 60B, 2507 (1927).
4) A.B. Schiotz, *Tids. Kemi. Farm. Terapi.*, 14, 270 (1917).
5) A.M. Ismail, and H.F. Harwood, *Analyst*, 62, 185 (1937).
6) A.C. Neish, *Chem. News*, 90, 196, 201 (1904).
7) T.C. Smith and C. James, *J. Amer. Chem. Soc.*, 34, 281 (1912).

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